



Chemical Kinetics Data Survey

VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised)

David Garvin, R. F. Hampson, Editors

Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

January 1974

Supersedes NBSIR 73-203 (May 1973)

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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VII. Tables of Rate and Photochemical Data for
Modelling of the Stratosphere (Revised)

Abstract

Chemical kinetic and photochemical data for gas phase reactions pertinent to the chemistry of the stratosphere are presented in four tables. These tables give recommended values and also cite recent experimental work. They give data in the following subject areas: chemical reactions and photochemistry of neutral species, energy transfer reactions, high temperature air reactions, and ion-molecule reactions.

Key words: atmospheric chemistry, chemical kinetics, data evaluation, energy transfer, gas phase, high temperature air chemistry, ion-molecule reactions, optical absorption cross sections, photochemistry, quantum yield, rate constants.

1. Introduction

This report consists of a set of tables of rate constants and photochemical data. These are preliminary tables designed for use in modelling of the stratosphere. They are being distributed now for interim use and for criticism by kineticists.

The tables are an extract from the chapter "Chemistry of the Stratosphere" by H. S. Johnston, P. J. Crutzen, R. J. Cvetanovic, M. L. Corrin, D. D. Davis, E. E. Ferguson, D. Garvin, R. F. Hampson, R. D. Hudson, L. J. Kieffer, H. I. Schiff and R. L. Taylor, in "The Natural Stratosphere" E. Reiter, editor, Climatic Impact Assessment Program Monograph No. 1. The present tables are essentially those in the version of this monograph which will be distributed in the Summer of 1974.

The first version of the table of data on the chemical reactions and photochemistry of neutral species was prepared by the Chemistry Panel on the Natural Stratosphere in December, 1972 at the Fort Lauderdale, Florida meeting and received limited distribution in the first preliminary draft of CIAP Monograph No. 1. A revised and expanded version was distributed in NBSIR 73-203 in May, 1973. This version incorporates changes and additions suggested at the meeting of the Chemistry Panel in Boulder, Colorado in October, 1973. From time to time, interim versions of this table have been distributed on a limited basis. Since October, 1973 the date of preparation has been given in the upper left hand corner of each page. The version of CIAP Monograph 1, to be distributed in 1974 has tables dated 12/3/73. This version distributed here dated January 4, 1974 supersedes all earlier versions. It is virtually the same as that dated 12/3/73.

The tables include contributions of rate evaluations by other scientists. These contributors represented in the present edition are D. L. Baulch, D. D. Drysdale and D. G. Horne, University of Leeds; J. Heicklen, Pennsylvania State University; A. C. Lloyd, University of California, Riverside; T. G. Slanger, Stanford Research Institute; J. Troe and K. Glanzer, Ecole Polytechnique Federale de Lausanne; K. H. Welge, York University; and W. H. Breckenridge, University of Utah.

The tables are in several parts:

- (1) Chemical reactions and photochemistry of neutral species (by the entire Chemistry Panel).
- (2) Vibrational energy transfer processes (R. Taylor).
- (3) High temperature air reactions (R. Taylor).
- (4) Ion-molecule reactions (E. E. Ferguson).

Bibliographies are included. These are also taken from the chapter. Occasionally the tables include comments that refer the reader to the text. This auxilliary information has not been included in this report.

It is the goal of the authors of these tables to provide recommended values for as many chemical processes pertinent to the stratosphere as possible. Where practical the basis of the recommendation has been made evident by citing recent experimental work.

But this is a preliminary selection. There may be pertinent work that has been omitted, incorrect citations of numbers, inadequate interpretation and even faulty recommendations. The reader will provide a valuable service by pointing these out to us and by suggesting better recommendations. Comments by readers have been helpful in improving these tables, and we would like to express our appreciation for them.

Correspondence about these tables should be sent either to David Garvin, B-152 Chemistry Building, National Bureau of Standards, Washington, D. C. 20234 or to H. S. Johnston, Department of Chemistry, University of California, Berkeley, California 94720.

2. Related Material

These tables rely heavily upon other modern data evaluation work. Some pertinent sources are summarized here.

Contributors to this data survey were mentioned in the introduction. Their evaluations are given in more detail in NBS Report 73-206 (May 1973).

Evaluations by a team of chemists at NBS have been published in J. Phys. Chem. Ref. Data 2, 267 (1973). Earlier versions of these evaluations had been distributed as NBS Report 10692 (January 1972) and NBS Report 10828 (April 1972). Additional evaluations have been published in NBSIR 73-207 (August 1973).

Evaluations by a group at the University of Leeds under the direction of D. L. Baulch have been published in "Evaluated Kinetic Data for High Temperature Reactions, volume 1, Homogeneous gas phase reactions of the H₂-O₂ system" D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, (Butterworths, London, 1972) and volume 2, "Homogeneous gas phase reactions of the H₂-N₂-O₂ system" D. L. Baulch, D. D. Drysdale and D. G. Horne, (Butterworths, London, 1973). Earlier evaluations by the same group have appeared in five reports from the Department of Physical Chemistry, University of Leeds, entitled "High Temperature Reaction Rate Data".

Data on reactions occurring in photochemical smog have been evaluated in "The Mechanism of Photochemical Smog Formation" by K. L. Demerjian, J. A. Kerr and J. G. Calvert (to appear in Advances in Environmental Science and Technology, J. N. Pitts, Jr. and R. L. Metcalf, editors, Wiley-Interscience, volume 4, 1974).

3. Needed Work

Although recommendations have been made for rate constants, absorption coefficients and quantum yields of many of the reactions thought to be important in the polluted stratosphere, much remains to be done. We will welcome suggestions of the best values to be used for any of the reactions denoted as not evaluated in the chemical reaction matrix immediately before Table I. These will be incorporated in the later versions of the tables. We will also welcome comments and corrections of any of the recommendations.

4. Tables from "The Natural Stratosphere" Climatic Impact Assessment Program Monograph No. 1, E. Reiter, editor

4.1 Chemical Reactions and Photochemistry of Neutral Species (Chemical Panel)

4.1.1 Introduction

These tables provide current (January, 1974) information on reaction rate constants, quantum yields and absorption cross sections. For many reactions, best estimates or recommended values are given. The reactions included in the tables are summarized on a "reaction grid" in section 4.1.4, Arrangement of the Tables. That grid also shows processes for which data (or data evaluations) are needed.

Most of the more important stratospheric reactions are in the tables. A number of the less important ones and some related systems are included, often simply for comparison.

The data have been selected by members of the Chemistry Panel and by other kineticists who have volunteered to review reactions of interest to them. Several principles have been used in the selection and presentation of data.

- (a) Where there is a recent published evaluation of the data and there are no newer data, the evaluation is adopted. The original data covered by the evaluation are not listed separately.
- (b) Where there is an evaluation but there are new data, both are listed and a preferred value is indicated (marked by an asterisk).
- (c) Where desirable, the available recent data sets are listed, and a selection is made or a preferred value is synthesized from them.

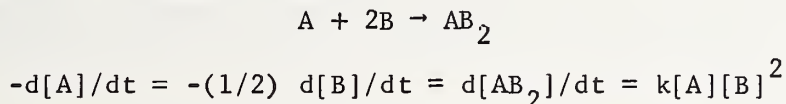
These selections are necessarily tentative because there is much current research on these atmospheric reactions. Indeed, we have often been influenced in making our selections by preliminary results that have been made available to us. As new data are published they will be incorporated in the tables. The persons making new selections or syntheses are usually identified by initials. These are either authors of the chapter or contributors identified below.

The Panel expresses its appreciation to scientists who have provided reports on their current work and who have suggested improvements. We are particularly indebted to those who have contributed evaluations of data: D. L. Baulch, D. D. Drysdale and D. G. Horne, University of Leeds; J. Heicklen, Pennsylvania State University; A. C. Lloyd, University of California, Riverside; T. G. Slanger, Stanford Research Institute; J. Troe and K. Glanzer, Ecole Polytechnique Federale de Lausanne; K. H. Welge, York University; and W. H. Breckenridge, University of Utah.

Earlier versions of these tables have appeared in the first draft of this Monograph (November 1972) and as NBSIR 73-203 (May 1973). Probably there will be future versions. The latest one should be used. Each is identified by a date on each page of the tables.

4.1.2 Conventions Concerning Rate Constants

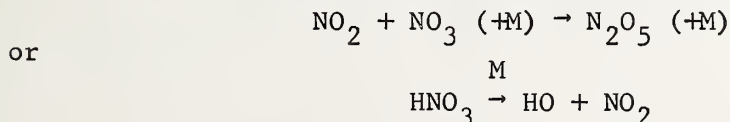
A. General Convention. Almost all of the reactions in the tables are elementary processes. For them the rate expression is derivable from a statement of the reaction, e.g.



Note that the stoichiometric coefficient for B, i.e. 2, appears in the denominator before B's rate of change (which is equal to $2k[A][B]^2$) as well as a power on the right hand side.

Wherever there may be any doubt an explicit rate expression is given.

B. Dissociation and Combination Reactions. Some reactions of these types are not of integral kinetic order over the stratospheric pressure and temperature range. That is, although they require an energy transfer agent, "M," they are in the "pressure fall-off region". For many such reactions we tabulate rate constants that include the effect of the energy transfer agent and give rates for various altitudes. The reactions are written to deemphasize "M," e.g.,



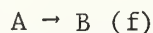
The rate expressions to be used do not have the concentration of M in them, e.g., Rate = $k[\text{NO}_2]$ $[\text{NO}_3]$ and $k[\text{HNO}_3]$ respectively. The units given for the k 's, s^{-1} for first order, and $\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ for second order, are consistent with this convention.

The altitude, temperature and number density regime used in these cases is

altitude/km	temp./K	$\log[M]/\text{molecule cm}^{-3}$
15	220	18.60
20	217	18.27
25	222	17.93
30	227	17.58
35	235	17.26
40	250	16.92
45	260	16.60

Except for the temperature at 15 km this table follows the U.S. standard atmosphere, 1962. In tables to be prepared in the future we intend to allow for observed temperature and number density variations at each altitude.

C. Forward and Reverse Reactions. In some cases there are no data on a reaction of interest but there are data on the "reverse" reaction. Occasionally, for



an evaluation will use the data on the "reverse" reaction together with an equilibrium constant to obtain the other rate constant. Obviously this is an approximation but it often is a useful method of estimating non-measured physical properties.

The tables contain notations to warn the reader when this procedure has been used, such as "based on reverse reaction," or when both reactions f and r are listed together " $k_f = k_r K_{eq}$ " or $k_r = k_f / K_{eq}$. These expressions, which are those used in the analyses, are based on equating the two rates at equilibrium:

$$R_f = R_r$$

$$k_f[A] = k_r[B]$$

$$K_{eq} = [B]/[A] = k_f/k_r.$$

4.1.3 Convention Concerning Optical Absorption Coefficients

These are reported in the tables as "absorption cross sections per molecule, base e" They are defined by the equations

$$I/I_0 = \exp(-\sigma[N]\ell)$$

$$\sigma = (1/([N]\ell)) \ln (I_0/I)$$

where I_0 and I are the intensities of incident and transmitted light, σ is the absorption cross section, $\text{cm}^2 \text{ molecule}^{-1}$, $[N]$ is the concentration of absorbers, molecules cm^{-3} , and ℓ is the path length, cm. Other definitions and units are frequently used. The terms "absorption coefficient" and "extinction coefficient" are common. It is always necessary to know what concentration units, path length units and type of logarithm (base e or base 10) are used in the definition. To convert "cross sections" to absorption coefficients in $(\text{atm at } 273 \text{ K})^{-1} \text{cm}^{-1}$, base e, multiply by 2.69×10^{19} .

4.1.4 Arrangement of the Table

A. Reaction Grid. The contents of the data table and the location of a reaction in it are shown on the "reaction grid," that follows this discussion.

This grid shows the molecules of interest for stratospheric chemistry along the top and left edges. The symbol "K" in the intersection for two reactants means that data for the reaction are in the table. Combination reactions, $A + B + M \rightarrow AB + M$ are above the main diagonal. Bimolecular reactions, typically $A + B \rightarrow C + D$, are below the diagonal.

B. Sequence of Reactions. The order in which reactions are listed follows the grid. All reactions of O atoms, the first species, shown in its row and column are listed first, then those of the second species, $\text{O}(\text{^1D})$, with all species other than O atoms, and so on. Thus a particular reaction is placed with the reactant highest (or to the left) on the grid. Bimolecular and combination reactions appear together.

The algorithm used to assign reaction locations is to construct an ordered ascending sequence of number pairs (or triplets), one for each reaction according to the following rules:

- (a) Assign numbers to each reactant in an equation. Use the numbers at the left side of the grid.
- (b) Arrange this set of numbers in ascending order, e.g. 1, 3 not 3, 1; 4, 10, 11 not 10, 11, 4

- (c) Order the sets in ascending order, giving priority to the lower number in the corresponding position of two sets being compared, e.g. 1,4; 1,7; 4,10,10; 4,10,11; 18, 24 etc. This completes the assignment of reaction sequence.

If a reaction is not filed according to this scheme, a cross reference appears at the proper spot. Exceptions are made principally to put forward and reverse reactions together.

C. Status of the Data. The reaction grid also shows what data are available and what are needed. A "dash" (-) means that the reaction may be ignored for stratospheric chemistry. An "O" means that data are needed or existing data should be evaluated. Often this means the reaction is important, but at times it means that data are required so that the importance of the reaction can be assessed. A blank inter-section merely means that no decision can be made at present. Finally, data are included in the table for some reactions that are unimportant. They are presented for comparison.

K = Data in table, O = Data selection or new data needed,
- = Unimportant for stratospheric chemistry, E = Data else-
where in the chapter, (Blank) = Role of process not assessed

[illegible]

Bimolecular Reactions: $A + B \rightarrow C + D + \dots$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ⁶ molecule ⁻² s ⁻¹	Notes and Reliability of log k
— O + O + M → O ₂ + M			
*Johnston (1968) review	1000 < T < 8000	3.80 x 10 ⁻³⁰ T ⁻¹ exp(-170/T)	M = O ₂ ±0.3
Campbell, Gray (1973)	298	4.8 x 10 ⁻³³	M = N ₂ ±0.03
	196	10.1 x 10 ⁻³³	±0.02
— O + O(¹ S) →		see O(¹ S) + O →	
— O(³ P) + O ₂ + M → O ₃ + M (f)			
— O ₃ + M → O + O ₂ + M (r)			
*This Survey (J.D.D. and D.G.)	200-346	6.6 x 10 ⁻³⁵ exp(510/T)	M = Ar ±0.7
		Rel. M efficiencies:	
		Ar(1.0) N ₂ (1.6) O ₂ (1.7) H ₂ O(15)	
Johnston (1968) eval.	200-1000	4.6 x 10 ⁻³⁵ exp(1050/T)	M = O ₃ ±0.1
		k _r = 1.65 x 10 ⁻⁹ exp(-11400/T) cm ³ molecule ⁻¹ s ⁻¹	±0.1
		Rel. M efficiencies: O ₃ (1.0), Ar(0.25), O ₂ (0.44), N ₂ (0.39)	
	200-346	6.6 x 10 ⁻³⁵ exp(510/T)	M = Ar
Hite, Herron, Davis (1972)		Rel. M efficiencies: Ar(1.0), He(0.9), N ₂ (1.7)	
	213-366	4.7 x 10 ⁻³⁵ exp(840/T)	M = Ar
Mulcahy, Williams (1968)		Rel. M efficiencies:	
		Ar(1.0) He(0.8) CO ₂ (3.4) O ₂ (1.1)	
Meaburn, et al (1968)	300	1.0 x 10 ⁻³³	M = CO ₂
		Rel. M efficiencies:	
		CO ₂ (1.0), CO(0.44), H ₂ O(0.88)	

(continued on next page)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of log k
Stuhl, Niki (1971)	300	$5.4 \times 10^{-34} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}$ M = N ₂ Rel. M efficiencies: N ₂ (1.0) O ₂ (1.18), CO(1.24)	
Donovan, Husain, Kirsch (1970)	300	$5.0 \times 10^{-34} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}$ M = Ar Rel. M efficiencies: Ar(1.0), Kr(0.98), He(0.92)	
Hippler, Troe (1971)	300	8×10^{-34} M = N ₂	
Slanger, Black (1970)	300	4.4×10^{-34} M = Ar, Rel. eff. Ar(1.0), N ₂ (1.6)	
Francis (1969)	300	1.24×10^{-34} M = O ₂	
Sauer (1967)	300	2.28×10^{-34} M = Ar	
— O + O ₂ + M → O ₃ * + M			
Bevan, Johnson (1973)	300	$5.4 \times 10^{-34} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}$ M = O ₂ Rel. efficiencies: O ₂ (1.0), Ar(0.50), N ₂ O(2.4), CO ₂ (2.5), SF ₆ (5.7) (a) Vibrationally excited O ₃ followed as fn. of time using absn. 250 < λ < 330nm.	(a)
— O(³ P) + O ₃ → O ₂ + O ₂			
Hampson (1973) eval.	220-1000	$1.9 \times 10^{-11} \text{ exp } (-2300/T)$	
*This Survey			
(D.D.D., H.I.S. and H.J.)	220-1000	$1.9 \times 10^{-11} \text{ exp } (-2300/T)$	±0.1 (a)
McCrumb, Kaufman (1972)	269-409	$1.1 \times 10^{-11} \text{ exp } (-2155/T)$	
Lundell, Ketcheson, Schiff (1969)	300	1.5×10^{-14}	
Husain, Kirsch, Donovan (1972)	300	1.3×10^{-14}	
Davis, Wong, Lephardt (1973)	220-353	$2.0 \times 10^{-11} \text{ exp } (-2280/T)$	
(a) The preferred value of this survey is based on the high temperature data included in Hampson (1973) and the low temperature data of McCrumb and Kaufman and of Davis, et al.			
Reactions of O with O ₂ and O ₃			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
— $\text{O} + \text{N} + \text{M} \rightarrow \text{NO} + \text{M}$			
*Baulch, et al (1973) review			
— $\text{O} + \text{NO} \rightarrow \text{N} + \text{O}_2$ (f)	200-400	$1.8 \times 10^{-31}(\text{T})^{-0.5} \text{cm}^3\text{molecule}^{-2}\text{s}^{-1}$, $\text{M} = \text{N}_2$	± 0.2
— $\text{O}_2 + \text{N} \rightarrow \text{NO} + \text{O}$ (r)			
*Baulch, et al (1973) review			
	1000-3000	$k_f = 2.5 \times 10^{-15} \text{T} \exp(-19500/\text{T})$	± 0.12 at 1000K (a)
	300-3000	$k_r = 1.1 \times 10^{-14} \text{T} \exp(-3150/\text{T})$	± 0.12 300<T<1500K
		(a) $k_f = k_r K_{\text{eq}}$. Error in log k increases to ± 0.3 at 3000K	
— $\text{O} + \text{NO} \rightarrow \text{NO}_2 + \text{h}\nu$			
Becker, et al (1973)	300	4.2×10^{-18}	
— $\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$ (f)			
— $\text{NO}_2 + \text{M} \rightarrow \text{NO} + \text{O} + \text{M}$ (r)			
*Baulch, et al (1973) review			
	200-500	$3.0 \times 10^{-33} \exp(940/\text{T}) \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$, $\text{M} = \text{O}_2$	± 0.08
		Rel. M efficiencies: $\text{O}_2(1.0)$, $\text{Ar}(1.0)$, $\text{N}_2(1.4)$	
	1400-2400	$k_r = 1.8 \times 10^{-8} \exp(-33000/\text{T}) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	± 0.1
		$\text{M} = \text{Ar}$	
Hampson, et al (1973a) review	200-500	accepts above recommendation	
Slanger, Wood, Black (1973)	296	6.0×10^{-32} $\text{M} = \text{Ar}$	(a)
	241	13.0×10^{-32} $\text{M} = \text{Ar}$	(a)
		(a) slightly higher but supports recommendation.	
— $\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M} + \text{h}\nu$			
Becker, et al (1973)	300	$7 \times 10^{-32} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$	

Reactions of O with N to NO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of $\log k$
— $\text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ (f)			
— $\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{O}$ (r)			
*This survey (D.D.D.)			
Baulch, et al (1973)	230-550	9.1×10^{-12}	± 0.06
	300-550	$k_f = 1.7 \times 10^{-11} \exp(-300/T)$	
		$k_r = k_f/K_{\text{eq}} = 2.8 \times 10^{-12} \exp(-23400/T)$	± 0.1
Davis, Herron and Huie (1972)	230-339	9.1×10^{-12}	
Clyne, Cruse (1971)	300	8.3×10^{-12}	
Harker, Johnston (1972)	300	9.2×10^{-12}	(a)
Clyne, Cruse (1972)	298	6.1×10^{-12}	
Slainger, et al (1973)	300	9.3×10^{-12}	(b)
	240	10.5×10^{-12}	
Hampson, et al (1973a) review	220-500	9.1×10^{-12}	± 0.08
Stuhl, Niki (1970)	300	4.4×10^{-12}	(b)
Bemand, Clyne, Watson (1973)	298-1055	$1.75 \times 10^{-10} \times (T)^{-0.52}$	
	298	$9.5 \pm 1.1 \times 10^{-12}$	
(a) $k/k(\text{O} + \text{NO} + \text{M})$ measured, where $k(\text{ref}) = 6.9 \times 10^{-32}$			
(b) Similar techniques were used by Slainger and by Stuhl and Niki:			
Flash photolysis - chemiluminescence.			
— $\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{NO}_3 + \text{M}$ (f)	298	$1.0 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2}\text{s}^{-1}$	± 0.2
— $\text{NO}_3 + \text{M} \rightarrow \text{NO}_2 + \text{O} + \text{M}$ (r)	296	$k_f = 6.3 \times 10^{-32}$	± 0.4
*Hampson, et al (1973a) review		$M = \text{N}_2$	
Baulch, et al (1973) review		$M = \text{N}_2$	
		$k_r \sim 8 \times 10^{-42} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$	(a)
		$M = \text{N}_2$	
		(a) No reliable data. Value based on k_f	

Reactions of O with NO₂

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of log k
— $\text{O} + \text{N}_2 \rightarrow \text{N} + \text{NO}$		See reverse reaction	
— $\text{O} + \text{N}_2 + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}$			
Baulch, et al (1973) review	1300-2500	$3.9 \times 10^{-35} \exp(-10400/T) \text{ cm}^3 \text{molecule}^{-2} \text{s}^{-1}$ $\text{M} = \text{Ar}$	± 0.2 (a)
	900-2100	$5.5 \times 10^{-15} \exp(-11330/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	± 0.2 (a,b)
		(a) $k_f = k_r^{\text{eq}}$	
		(b) 2d order high pressure limit	
— $\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}$			
Baulch, et al (1973) review	1300-2500	$8.3 \times 10^{-10} \exp(-29000/T) \text{ M} = \text{Ar}$	± 0.2
	900-2100	$1.3 \times 10^{+11} \exp(-30000/T) \text{ s}^{-1}$	± 0.2 (a)
		(a) first order high pressure limit	
— $\text{O} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$ (1)			
— $\text{O} + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO}$ (2)			
— $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}$ (2r)			
Baulch, et al (1973) review	1200-2000	$k_1 = 1.7 \times 10^{-10} \exp(-14.1 \times 10^3/T)$	± 0.4 (a)
		$k_2 = 1.7 \times 10^{-10} \exp(-14.1 \times 10^3/T)$	± 0.3
	1200-2000	$k_{2r} = 2.2 \times 10^{-12} \exp(-32100/T)$	± 0.3 (b)
		(a) Based on $k_1/k_2 = 1$	
		(b) $d[\text{NO}]/dt = -2k_{2r}[\text{NO}]^2$	
— $\text{O} + \text{N}_2\text{O}_5 \rightarrow \text{products}$			
Davis (1973)	300	$< 2 \times 10^{-13}$	preliminary
— $\text{O} + \text{NH}_2 \rightarrow \text{HNO} + \text{H}$ (a)			
$\rightarrow \text{HO} + \text{NH}$ (b)			
Gehring, et al (1973)	300	$3.5 \times 10^{-12} (k_a + k_b)$	

Reactions of O with N_2 to NH_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $\text{k/cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of log k
— $\text{O} + \text{NH}_3 \rightarrow \text{HO} + \text{NH}_2$ (f)			
— $\text{HO} + \text{NH}_2 \rightarrow \text{O} + \text{NH}_3$ (r) Baulch, et al (1973) review	300-1000	$k_f = 2.5 \times 10^{-12} \exp(-3020/T)$	± 0.2
*Kurylo, et al (1969) (D.G.) Albers, et al (1969) Kondratiev (1970) review	300-1000 361-677 300-1000 350-1000	$k_r = k_f/K_{\text{eq}} = 1 \times 10^{-13}$ $k_f = 6.6 \times 10^{-12} \exp(-3300/T)$ $k_f = 2 \times 10^{-12} \exp(-3000/T)$ $k_f = 1.8 \times 10^{-12} \exp(-2500/T)$	± 0.2 (a) ± 0.3
Data of Albers, et al provide an upper limit when extrapolated to 220K (a) $\text{HO} + \text{NH}_2 \rightarrow \text{NH} + \text{H}_2\text{O}$ may be preferred channel.			
— $\text{O} + \text{H} + \text{M} \rightarrow \text{HO} + \text{M}$ Schofield (1973) review Baulch, et al (1972) review	1000-3000	$-2 \times 10^{-32} \text{ cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ M = Ar No recommendation	± 1 estimate
— $\text{O} + \text{HO} \rightarrow \text{H} + \text{O}_2$ (f) — $\text{O}_2 + \text{H} \rightarrow \text{O} + \text{HO}$ (r) Baulch, et al (1972) review *Baulch, et al (1972) review *Wilson (1972) review	300 700-2500 300-2000	$k_f = 3.8 \pm 1.7 \times 10^{-11}$ $k_r = 3.7 \times 10^{-10} \exp(-8450/T)$ $k_f = 4.2 \pm 1.7 \times 10^{-11}$	± 0.17 ± 0.1 ± 0.3
— $\text{O} + \text{HO} + \text{M} \rightarrow \text{HO}_2 + \text{M}$ Baulch, et al (1972) review		no recommendation	
— $\text{O} + \text{HO}_2 \rightarrow \text{HO} + \text{O}_2$ Lloyd (1973) review	-300	$8 \times 10^{-11} \exp(-500/T)$	estimate
— $\text{O} + \text{H}_2 \rightarrow \text{HO} + \text{H}$ (r) — $\text{H} + \text{HO} \rightarrow \text{O} + \text{H}_2$ (r) Baulch, et al (1972) review	400-2000	$k_f = 3.0 \times 10^{-14} (T) \exp(-4450/T)$ $k_r = k_f/K_{\text{eq}} = 1.4 \times 10^{-14} (T) \exp(-3500/T)$	± 0.1 ± 0.15

Reactions of O with NH_3 to H_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of log k
— $\text{O} + \text{H}_2\text{O} \rightarrow \text{HO} + \text{HO}$		See reverse reaction	
— $\text{O} + \text{H}_2\text{O} \rightarrow \text{H} + \text{HO}_2$		no recommendation	
Baulch, et al (1972) review			
— $\text{O}(\text{}^3\text{P}) + \text{H}_2\text{O}_2 = \text{HO}_2 + \text{OH}$ (a) = $\text{H}_2\text{O} + \text{O}_2$ (b)			
*This Survey (D.D.D.)			
Foner, Hudson (1962)	283-373	$k(a+b) = 2.75 \times 10^{-12} \exp(-2125/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	± 0.07 (a)
Davis (1973)	300	$\leq 4 \times 10^{-15}$	
	283-373	$k(a+b) = 2.75 \times 10^{-12} \exp(-2125/T)$	± 0.06
	(a)	There is presently no basis for assigning relative k values to the two possible channels for this reaction.	
— $\text{O} + \text{HNO}_2 \rightarrow \text{HO} + \text{NO}_2$		No data. Probably faster than $\text{O} + \text{HNO}_3$, since it is 94 kJ/mol more exothermic.	
This survey (D.G.)		No recommendation	
Baulch, et al (1973) review			
— $\text{O} + \text{HNO}_3 \rightarrow \text{HO} + \text{NO}_3$	300	$< 1.5 \times 10^{-14}$	
*Hampson, et al (1973) review	300	$< 1.3 \times 10^{-14}$	
Morley, Smith (1972)	300	$< 1 \times 10^{-16}$	
Wayne (1973)	300	$< 10^{-14}$	approximate upper limit
Baulch, et al (1973) review			
— $\text{O} + \text{SO}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}$	250-1000	$1 \times 10^{-33} \exp(+500/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$, $\text{M} = \text{O}_2$, N_2 , Ar, He	± 0.3 at 300K ± 0.6 at other temp.
Schofield (1973) review			
*Davis (1973) (D.D.D., D.G.)	220-353	$3.4 \times 10^{-32} \exp(-1130/T)$	$\text{M} = \text{N}_2$
Reactions of O with H_2O to SO_2		$\text{N}_2(1.0)$, He(.45), Ar(.87), $\text{SO}_2(56)$	

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
— $\text{O} + \text{SO}_3 \rightarrow \text{SO}_2 + \text{O}_2$ Schofield (1973) review	1480-1550	$5 \times 10^{-10} \exp(-6000/T)$	Uncertain
Jacob, Winkler (1972)	300-500	$3 \times 10^{-16} \exp(-500/T)$	
— $\text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2$ Watson (1973) review	300	$5.3 \pm 0.8 \times 10^{-11}$	± 0.1
— $\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$ Watson (1973) review	300	5×10^{-13}	± 0.2
— $\text{O} + \text{CHO} \rightarrow \text{CO}_2 + \text{H} \text{ (a)}$ $\rightarrow \text{CO} + \text{HO} \text{ (b)}$ *Washida, et al (1973)	297	$2.1 \pm 0.4 \times 10^{-10} (k_a + k_b)$	
— $\text{O} + \text{CH}_2\text{O} \rightarrow \text{CHO} + \text{OH}$ *Demerjian, et al (1972) review	300	1.6×10^{-13}	
Mack, Thrush (1973)	300	1.5×10^{-13}	± 0.05
— $\text{O} + \text{CH}_3 \rightarrow \text{CH}_2\text{O} + \text{H} \text{ (a)}$ $\rightarrow \text{CHO} + \text{H}_2 \text{ (b)}$ Washida, Bayes (1973)	300	$k_a = 1.23 \times 10^{-10}$	± 0.1
Washida, et al (1973)	300	k_b negligible $k_b/k_a < 0.05$	
Morris, Niki (1972)	300	$k_a = 9 \times 10^{-11}$	
Peeters, Mahnen (1973)	1100-1900	$k_a = 2.2 \times 10^{-10} \exp(-1000/T)$	
— $\text{O} + \text{CH}_4 \rightarrow \text{products}$ *Herron, Hule (1972) review	350-1000	$3.5 \times 10^{-11} \exp(-4550/T)$	± 0.11
— $\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{products}$ *Herron, Hule (1972) evaluation	200-500	$5.5 \times 10^{-12} \exp(-565/T)$	± 0.08
Reactions of O with SO_3 to C_2H_4			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of log k
— $\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{products}$			
*Herron, Huie (1972) evaluation	300-650	$4.1 \times 10^{-11} \exp(-3200/T)$	± 0.11
— $\text{O} + \text{C}_3\text{H}_8 \rightarrow \text{products}$			
*Herron, Huie (1972) evaluation	200-500	$4.1 \times 10^{-12} \exp(-38/T)$	± 0.08
— $\text{O}(^1\text{D}_2) + \text{O}_2 \rightarrow \text{O}_2(^1\Sigma_g^+) + \text{O}(^3\text{P})$	298	$7.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{O}_3 \rightarrow \text{O}_2(^3\Sigma_g^-) + \text{O}_2(^1\text{D}_2) \text{ (?) (a)}$	"	$5.3 \times 10^{-10} (k_a + k_b) k_a/k_b \sim 1$	± 0.3 a,c
— $\rightarrow \text{O}_2 + 2\text{O}(^3\text{P}) \text{ (b)}$	"		
— $\text{O}(^1\text{D}_2) + \text{NO} \rightarrow \text{NO} + \text{O}(^3\text{P})$	"	1.7×10^{-10}	± 0.3 a
— $\text{O}(^1\text{D}_2) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	"	2.8×10^{-10}	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{N}_2 \rightarrow \text{N}_2 + \text{O}(^3\text{P})$	"	5.4×10^{-11}	± 0.15 a
— $\text{O}(^1\text{D}_2) + \text{N}_2 + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}$	"	$2.8 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	b
— $\text{O}(^1\text{D}_2) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 \text{ (a)}$	"	$1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	± 0.1 a
— $\rightarrow 2\text{NO} \text{ (b)}$	"	1.1×10^{-10}	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{NH}_3 \rightarrow \text{NH}_2 + \text{HO}$	298	(Probably about 3×10^{-10})	a,d
— $\text{O}(^1\text{D}_2) + \text{H}_2 \rightarrow \text{HO} + \text{H}$	"	No measurements available)	
— $\text{O}(^1\text{D}_2) + \text{H}_2\text{O} \rightarrow 2\text{HO}$	"	2.9×10^{-10}	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{H}_2\text{O}_2 \rightarrow \text{HO} + \text{HO}_2$	"	3.5×10^{-10}	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{CO} \rightarrow \text{CO} + \text{O}(^3\text{P})$	"	$> 3 \times 10^{-10}$	d
— $\text{O}(^1\text{D}_2) + \text{CO}_2 \rightarrow \text{CO}_2 + \text{O}(^3\text{P})$	"	7.7×10^{-11}	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HO} \text{ (a)}$	"	1.8×10^{-10}	± 0.1 a
— $\rightarrow \text{CH}_2\text{O} + \text{H}_2 \text{ (b)}$	"	$4.0 \times 10^{-10} (k_a + k_b) k_a/k_b = 10$	± 0.1 a
— $\text{O}(^1\text{D}_2) + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HO} \text{ (a)}$	"	$4.8 \times 10^{-10} (k_a + k_b)$	± 0.1 a
— $\rightarrow \text{CH}_3 + \text{CH}_2\text{OH} \text{ (b)}$	"		

(notes are on next page)

Reactions of O with C_2H_6 and C_3H_8 and of $\text{O}(^1\text{D})$

Notes and
Reliability of
log k

Reaction/Reference
* = Preferred Value

Temp.
Range/K

Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹

a. *Evaluation for this survey (R.J.C.). See details in text "Reactions of O(¹D₂) Atoms."

b. Gaedke, et al (1972)

c. Further determinations are desirable. See details of evaluation.

d. Estimated, Experimental determination is necessary.

— O(¹ S) + O(³ P) → ?	300	7.5 x 10 ⁻¹²	±0.2	a
— O(¹ S) + O ₂ → ?	200-377	4.3 x 10 ⁻¹² exp(-850/T)	±0.15	a
— O(¹ S) + O ₃ → ?	300	5.8 x 10 ⁻¹⁰	±0.07	a
— O(¹ S) + NO → ?	200-291	3.2 x 10 ⁻¹¹ (T) ^{0.5}	±0.05	a
— O(¹ S) + NO ₂ → ?	300	5 x 10 ⁻¹⁰	±0.2	a
— O(¹ S) + N ₂ → ?	200-380	< 5 x 10 ⁻¹⁷		a
— O(¹ S) + N ₂ O → ?	300	1.4 x 10 ⁻¹¹	±0.1	a
— O(¹ S) + NH ₃ → ?	300	5 x 10 ⁻¹⁰	±0.2	a
— O(¹ S) + H ₂ O → ?	300	> 10 ⁻¹⁰	±1	a
— O(¹ S) + CO ₂ → ?	200-450	3.1 x 10 ⁻¹¹ exp(-1320/T)	±0.15	a
— O(¹ S) + CH ₄ → ?	300	2 x 10 ⁻¹⁴	±0.4	a

a) Rate constants evaluated for this survey

by T. G. Slanger and K. H. Welge

Reactions of O(¹S)

Notes and
Reliability of
log k

Reaction/Reference
* = Preferred Value

Temp.
Range/K

Reaction Rate Constant
 $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

— $\text{O}_2 + \text{h}\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P})$ Hampson, et al (1973a) review		$\phi = 1$	$175 < \lambda < 200 \text{ nm}$	
— $\text{O}_2 + \text{h}\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{D})$ Hampson, et al (1973a) review		$\phi = 1$	$133 < \lambda < 175 \text{ nm}$	
— $\text{O}_2 + \text{h}\nu \rightarrow 2 \text{ oxygen atoms}$ Hampson, et al (1973a) review		$\phi = 1$	$106 < \lambda < 200 \text{ nm}$	
— $\text{O}_2 + \text{h}\nu$ Hampson, et al (1973a) review				
— $\text{O}_2 + \text{N} \rightarrow \text{NO} + \text{O}$				
— $\text{O}_2 + \text{NO} + \text{NO} \rightarrow \text{NO}_2 + \text{NO}_2$ *Baulch, et al (1973) review	273-660			
Stedman, Niki (1973)	300			
— $\text{O}_2 + \text{NO} + \text{NO}_2 \rightarrow \text{NO}_2 + \text{NO}_3$				± 0.2
— $\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{O}$				± 0.1

Recommended values of absorption cross section

$135 < \lambda < 243 \text{ nm}$

see reverse reaction

$3.3 \times 10^{-39} \exp(530/T) \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$

$k_1 [\text{NO}]^2 [\text{O}_2] = -(1/2) d[\text{NO}]/dt$

2.0×10^{-38}

where $d[\text{NO}_2]/dt = 2k[\text{NO}]^2 [\text{O}_2]$

see reverse reaction

see reverse reaction

Reactions of O_2 with $\text{h}\nu$ to NO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
— $\text{O}_2 + \text{NO} + \text{M} \rightarrow \text{NO}_3 + \text{M}$ Baulch, et al (1973) review		No recommendation	
— $\text{O}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_3$		see reverse reaction	
— $\text{O}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_3$		see reverse reaction	
— $\text{O}_2 + \text{N}_2 \rightarrow \text{N}_2\text{O} + \text{O}$ *Baulch, et al (1973) review	1200-2000	$1.0 \times 10^{-10} \exp(-55.2 \times 10^3/T)$ (a) $k_f = k_r/K_{eq}$ see reverse reaction	+0.4 (a)
— $\text{O}_2 + \text{H} \rightarrow \text{HO} + \text{O}$			
— $\text{O}_2 + \text{H} + \text{M} \rightarrow \text{HO}_2 + \text{M}$ *This Survey (D.D.D.)	203-404	$6.7 \times 10^{-33} \exp(290/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $M = \text{Ar or He}, k(300) = 1.8 \times 10^{-32}$ Rel. M efficiencies: Ar(1.0), He(1.0), N_2 (3.1), O_2 (3.1), H_2O (25) (a) This evaluation is base on the 300 K data reviewed by Baulch, et al. (1972) and the recent studies by Hikida, et al (1971), Kurylo (1972) and Wong and Davis (1972).	±0.7 (a)
Baulch, et al (1972) eval.	300-2000	$4.1 \times 10^{-33} \exp(500/T) M = \text{Ar}$	±.2
Bishop, Dorfman (1970)	300	Rel. M efficiencies: Ar(1.0), He(1.0), N_2 (1.3), O_2 (1.3), H_2O (21)	
Hikida, Eyre, Dorfman (1971)	300	$2.35 \times 10^{-32} M = \text{Ar}$	
Ahumada, Michael, Osborne (1972)	300	$1.64 \times 10^{-32} M = \text{Ar}$	
	300	$0.75 \times 10^{-32} M = \text{He}$	
Allen, Moortgat (1973)	115-300	Rel. M efficiencies: He(1.0), Ar(0.8)	
		$1.4(+0.14) \times 10^{-33} \exp(+700/T), M = \text{Ar}$	
Kurylo (1972)		Rel. M efficiencies at 297K: Ar(1.0), He(0.97), H_2 (1.28).	
(continued on next page)			
Reactions of O_2 with NO to H	203-404	$6.7 \times 10^{-33} \exp(235/T)$	

Notes and
Reliability of
log k

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
Wong, Davis (1973)	220-360	Rel. M efficiencies: Ar(1.0), He(1.0), N ₂ (3.4) 6.8 x 10 ⁻³³ exp(340/T) Rel. M efficiencies: Ar(1.0), He(0.93) N ₂ (2.8), H ₂ (3.0), CH ₄ (21.5) 1.9 x 10 ⁻³² M = Ar or He see reverse reaction	
Westenberg, DeHaas (1972)	300	no recommendation	
— O ₂ + H ₂ → H + HO ₂		no recommendation	
— O ₂ + H ₂ → HO + HO		no recommendation	
Baulch, et al (1972) review		no recommendation	
— O ₂ + H ₂ O → HO ₂ + HO		no recommendation	
Baulch, et al (1972) review		no recommendation	
— O ₂ + H ₂ O ₂ → HO ₂ + HO ₂		no recommendation	
Baulch, et al (1972) review		no recommendation	
— O ₂ + HNO → NO + HO ₂		no recommendation	
Demerjian, et al (1972) review	~00	< 2.1 x 10 ⁻²⁰ , E/R > 5000K	estimated
— O ₂ + SO → SO ₂ + O			
*Breckenridge, Miller (1972) (VHB) 300	< 8 x 10 ⁻¹⁷		
*Schofield (1973) review (VHB)	400-2500	3.0 x 10 ⁻¹³ exp (-2800/T)	+0.3
— O ₂ + CHO → CO + HO ₂			
Demerjian, et al (1972) review	300	1.7 x 10 ⁻¹³	estimated
Peeters, Mahnen (1973)	1400-1800	5 x 10 ⁻¹¹	
*Washida, et al (1973)	297	k/k(O + CHO) = 2.74 ± 0.21 x 10 ⁻² yielding k = 5.7 ± 1.2 x 10 ⁻¹²	

Reactions of O₂ with H₂ to CHO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
— O ₂ + CH ₃ → CH ₃ O + HO			
Basco, et al (1972)	295	3 x 10 ⁻¹⁶	estimated (a)
a. Based on negative result and sensitivity limit. Other measurements at higher T suggest an appreciable activation energy.			
— O ₂ + CH ₃ + M → CH ₃ O ₂ + M			
Basco, et al (1972) (D.G.)	295	2.6 x 10 ⁻³¹ , cm ⁶ molecule ⁻² sec ⁻¹ , M = N ₂ (low pressure limit)	
— O ₂ + CH ₃ (+M) → CH ₃ O ₂			
Basco, et al (1972) (D.G.)	295	4.3 x 10 ⁻¹³ , cm ³ molecule ⁻¹ s ⁻¹ , M = N ₂ , (2d order high pressure limit.) k = 1.7 x 10 ⁻¹³ , M = N ₂ , at 30 torr.	
— O ₂ + CH ₃ O → . . .		see CH ₃ O + O ₂	
— O ₂ (¹ Δ) + M → O ₂ + M			
*Hampson (1973) review	285-322	2.2 x 10 ⁻¹⁸ (T/300) ^{0.8} , M = O ₂	±0.1
	300	< 2 x 10 ⁻²⁰ , M = N ₂	
Collins, et al (1973)	300	1.4 x 10 ⁻¹⁹ , M = N ₂	±0.06
*Breckenridge, Miller (1972) (WHB)	300	< 2 x 10 ⁻¹⁵ M = SO ₂	(a)
Fisher, McCarty (1966) (WHB)	300	< 3 x 10 ⁻¹⁶ M = CO	(a)
		(a) total rate, quenching and reaction	
— O ₂ (¹ Δ) + O ₃ → 2O ₂ + O			
Clark, Jones, Wayne (1970)	195-439	6.6 x 10 ⁻¹³ exp(-1560/T)	±0.24
Findlay, Snelling (1971)	283-321	4.5 x 10 ⁻¹¹ exp(-2830/T)	±0.11
Becker, et al (1972)	296-360	6.0 x 10 ⁻¹¹ exp(-2850/T)	±0.17
Collins, et al (1973)	300	4.4 x 10 ⁻¹⁵	±0.11
Schofield (1972) review	283-321	4.5 x 10 ⁻¹¹ exp(-2830/T)	±0.11
Reactions of O ₂ with CH ₃ and of O ₂ (¹ Δ)			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $\text{K/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of $\log k$
— $\text{O}_2(^1\Delta) + \text{SO} \rightarrow \text{O}_2 + \text{SO}(^1\Delta)$ Breckenridge, Miller (1972) (WHB)	300	$3.5 \pm 0.36 \times 10^{-13}$	
— $\text{O}_2(^1\Sigma) + \text{M} \rightarrow \text{O}_2 + \text{M}$ *Hampson (1973) review	300	1.5×10^{-16} , $\text{M} = \text{O}_2$ 2.0×10^{-15} , $\text{M} = \text{N}_2$ 4×10^{-12} , $\text{M} = \text{H}_2\text{O}$	± 0.12 ± 0.1 ± 0.18
— $\text{O}_3 + \text{h}\nu \rightarrow \text{O}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$ *Hampson, et al. (1973) review		$\phi = 1$, $450 < \lambda < 750 \text{ nm}$ - Chappuis bands $\phi = 0$, $250 < \lambda < 350 \text{ nm}$ $k = 3.39 \times 10^{-4} \text{ s}^{-1}$ (Daylight) ($450 < \lambda < 750 \text{ nm}$ - Chappuis bands)	
Johnston (1973)			
— $\text{O}_3 + \text{h}\nu \rightarrow \text{O}(^3\text{P}) + \text{O}_2(^1\Delta \text{ or } ^1\Sigma)$ *Hampson, et al. (1973) review		$\phi = 1$, $310 < \lambda < 350 \text{ nm}$ - Huggins bands $\phi = 0$, $\lambda < 310 \text{ nm}$	
— $\text{O}_3 + \text{h}\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\Delta)$ *Hampson, et al. (1973) review		$\phi = 1$, $250 < \lambda < 310 \text{ nm}$ - Hartley bands $\phi = 0$, $\lambda > 310 \text{ nm}$	
Lin, DeMore (1973)		Results consistent with above recommendation.	
— $\text{O}_3 + \text{h}\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\Sigma_g^+)$ *Hampson, et al. (1973) review		$\phi = 0$, $250 < \lambda < 350 \text{ nm}$ see reverse reaction	
— $\text{O}_3 + \text{M} \rightarrow \text{O} + \text{O}_2 + \text{M}$ — $\text{O}_3 + \text{N} \rightarrow \text{NO} + \text{O}_2$ *Baulch, et al (1973) review	300	5.7×10^{-13}	± 0.2

Reactions of $\text{O}_2(^1\Delta)$ with SO to O_3 with M

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of log k
— $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ (f)			
— $\text{O}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_3$ (r)			
*Hampson, et al (1973) review	198-330	$k_f = 9 \times 10^{-13} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	± 0.11
Stedman, Niki (1973)	298	$k_f = 1.73 \pm 0.1 \times 10^{-14}$	± 0.2
Baulch, et al (1973) review	200-350	$k_f = 1.5 \times 10^{-12} \exp(-1330/T)$	± 0.2
Ghormley, et al (1973)	200-350	$k_r = k_f/K_{\text{eq}} = 2.8 \times 10^{-12} \exp(-25400/T)$	± 0.2
Bemand, et al (1973)	298	$k_f = 1.41 \times 10^{-14}$	± 0.01 precision
— $\text{O}_3(001) + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	300	$1.81 \pm 0.13 \times 10^{-14}$	
Gordon, Lin (1973)	300	2.5×10^{-13}	(a)
Kurylo, et al (1973)	300	2.2×10^{-13}	(a)
		(a) Rate -20 times faster than with $\text{O}_3(000)$.	
		$\text{O}_3(010)$ may be reactive species	
— $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$ (f)			
— $\text{O}_2 + \text{NO}_3 \rightarrow \text{O}_3 + \text{NO}_2$ (r)			
*This survey (D.D.D., D.G.)	220-340	$k_f = 1.1 \times 10^{-13} \exp(-2450/T)$	± 0.1
Hampson, et al (1973) review	298	$k_f = 5 \times 10^{-17}$	± 0.2
Johnston, Yost (1949)	286-302	$k_f = 9.8 \times 10^{-12} \exp(-3500/T)$	
Baulch, et al (1973) review	286-302	$k_f = 9.8 \times 10^{-12} \exp(-3500/T)$	± 0.3
	300	$k_r = 7 \times 10^{-34}$ based on k_f	± 0.3
Wu, Morris, and Niki (1973)	299	$k_f = 4.4 \times 10^{-17}$	± 0.06 (a)
Ghormley, et al (1973)	298	$k_f = 3.2 \times 10^{-17}$	± 0.07
Davis (1973)	260-343	$k_f = 1.0 \times 10^{-13} \exp(-2420/T)$	± 0.2
Johnston (1973)	231-268	$k_f = 1.23 \times 10^{-13} \exp(-2470/T)$	
Stedman, Niki (1973)	298	$k_f = 6.5 \pm 0.8 \times 10^{-17}$	

(note on next page)

 Reactions of O_3 with NO and NO_2

Notes and
Reliability of
log k

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
(a) Revision, based on later experiments of value reported by Stedman and Niki (1973)			
— O ₃ + H → HO + O ₂			
*Hampson, et al (1973) review	300	2.6 x 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹	±0.1 ?
— O ₃ + HO → HO ₂ + O ₂			
DeMore (1973)	300	8 x 10 ⁻¹⁴	
Anderson, Kaufman (1973)	220-450	1.3 x 10 ⁻¹² exp(-956/T)	
*Hampson, et al (1973) review	220-450	1.6 x 10 ⁻¹² exp(-1000/T)	±0.3
Davis (1973)	298	7.4 x 10 ⁻¹⁴	±0.06
Kurylo (1973)	298	6.5 x 10 ⁻¹⁴	±0.06
— O ₃ + HO(v ₁ > 0) → products			
Coltharp, Worley, Potter (1971)	300	v ₁ (HO) k/cm ³ molecule ⁻¹ s ⁻¹	
	2	1.9 ± 1.1 x 10 ⁻¹²	
	3	2.4 ± 0.9 x 10 ⁻¹²	
	4	2.8 ± 0.8 x 10 ⁻¹²	
	5	3.4 ± 0.7 x 10 ⁻¹²	
	6	5.3 ± 0.6 x 10 ⁻¹²	
	7	6.5 ± 0.5 x 10 ⁻¹²	
	8	6.7 ± 0.5 x 10 ⁻¹²	
	9	7.7 ± 0.3 x 10 ⁻¹²	
— O ₃ + HO ₂ → (HO + 2O ₂)			
DeMore (1973)	300	3 x 10 ⁻¹⁵	
Anderson (1973)	220-450	k/k(HO + O ₃ → HO ₂ + O ₂) ≤ 0.1	
*This Survey (D.G.) (continued on next page)	225-298	1 x 10 ⁻¹³ exp(-1250/T)	±0.3 a

Reactions of O₃ with H to HO₂

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of log k
Lloyd (1973) review	200-500	$1.7 \times 10^{-13} \exp(-1400/T)$	$> \pm 0.3$ a, b
Simonaitis, Heicklen (1973)	225-298	$k/(k_{\text{ref}})^{0.5} = 1.9 \times 10^{-8} \exp(-1000/T)$ $(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{0.5}$	± 0.15 a
(a) Reference reaction: $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. Preferred value is based on meas. of Simonaitis and Heicklen and k_{ref} given in these tables.			
(b) Pre-exponential factor increased			
$\text{O}_3 + \text{SO} \rightarrow \text{O}_2 + \text{SO}_2$ Schofield (1973) review	223-303	$2.5 \times 10^{-12} \exp(-1050/T)$	± 0.5
$\text{O}_3 + \text{Cl} \rightarrow \text{ClO} + \text{O}_2$ Watson (1973) review	300	$1.95 \pm 0.35 \times 10^{-11}$	± 0.1
$\text{O}_3 + \text{CO} \rightarrow \text{CO}_2 + \text{O}_2$ Arin, Varneck (1972)	296	$< 4 \times 10^{-25}$	
$\text{O}_3 + \text{CH}_4 \rightarrow \text{products}$ Dilleuth, et al (1960)	310-340	$2.7 \times 10^{-13} \exp(-7700/T)$	
$\text{O}_3 + \text{C}_2\text{H}_4 \rightarrow \text{products}$ Demerjian, et al (1972) review DeMore (1969)	300	2.7×10^{-18}	
Stedman, et al (1973)	178-233	$3.2 \times 10^{-15} \exp(-2400/T)$	
*This survey (D.G., R.H.)	300	$1.55 \pm 0.15 \times 10^{-18}$	
	200-300	$6 \times 10^{-15} \exp(-2400/T)$	(a)
(a) The room temperature recommendation of Demerjian et al and the value of Stedman et al have been combined with DeMore's activation energy.			

Reactions of O_3 with SO to C_2H_4

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $\text{k/cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of $\log k$
— $\text{O}_3 + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_5\text{O}_3$			
Demerjian et al (1972) review	300	1.0×10^{-17}	
DeMore (1969)	183, 193, 300	$1.65 \times 10^{-15} \exp (-1600/\text{T})$	(b)
Stedman, et al (1973)	300	$1.25 \pm 0.1 \times 10^{-17}$	
*This survey (D.G., R.H.)	200-300	$7 \times 10^{-15} \exp (-1900/\text{T})$	(a)
	(a)	The room temperature value of Stedman et al has been combined with DeMore's low temperature data.	
	(b)	Includes 300K point of Hanst et al (1959)	

Reactions of O_3 with C_3H_6

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of $\log k$
— $\text{N} + \text{N} + \text{M} \rightarrow \text{N}_2 + \text{M}$			
*Baulch, et al (1973) review	100-600	$8.3 \times 10^{-34} \exp(+500/T) \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}$, ($\text{M} = \text{N}_2$)	± 0.2 (200-600)
— $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} (f)$		where $-d[\text{N}]/dt = 2k[\text{N}]^2 [\text{M}]$	< 0.2 ($T < 200\text{K}$)
— $\text{O} + \text{N}_2 \rightarrow \text{N} + \text{NO} (r)$			
*Baulch, et al (1973) review	300-5000	$k_f = 2.7 \times 10^{-11}$	± 0.1 (a)
	2000-5000	$k_r = 1.3 \times 10^{-10} \exp(-39000/T)$	± 0.3
		(a) Uncertainty increases to ± 0.3 for $T > 2000$. k_f based on 300 K data and $k_r(T > 2000)$.	
— $\text{N} + \text{NO}_2 \rightarrow$ all channels			
*Baulch, et al (1973) review	300	1.85×10^{-11}	
		no reliable estimate can be made for the relative importance of the four product channels:	
		$\rightarrow \text{NO} + \text{NO}, \rightarrow \text{N}_2\text{O} + \text{O}, \rightarrow \text{N}_2 + \text{O}_2, \rightarrow \text{N}_2 + \text{O} + \text{O}$	
— $\text{N} + \text{HO} \rightarrow \text{NO} + \text{H}$			
*Baulch, et al (1973) review	300	5.3×10^{-11}	± 0.3 (a)
— $\text{NO} + h\nu$			
Hampson, et al (1973a) review		(a) Based on $k/k(\text{O} + \text{HO} \rightarrow \text{O}_2 + \text{H}) = 1.4$	
		Recommended values of oscillator strengths from which absorption cross sections can be derived are given for β , γ , δ , and ϵ bands. Recommended values of absorption cross section $106 < \lambda < 135 \text{ nm}$. No recommended quantum yield values.	
Reactions of $\text{N} + \text{N}$ to $\text{NO} + h\nu$			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $\text{k/cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of log k
— $\text{NO} + \text{H} \rightarrow \text{N} + \text{O} + \text{H}$			
*Baulch, et al (1973) review	4200-6700	Insufficient data for a reliable recommendation. Use, with caution: $6.6 \times 10^{-4} T^{-1.5} \exp(-75.5 \times 10^3/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ (M = Ar, O ₂ , N ₂) $k(\text{M} = \text{NO}, \text{N}, \text{O})/k(\text{Ar}) \sim 18$	
— $\text{NO} + \text{NO} \rightarrow \text{N} + \text{NO}_2$			
Baulch, et al (1973) review		Endothermic. Unimportant compared to $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}$ see reverse reaction see O ₂ + NO + NO $\rightarrow$ NO ₂ + NO ₂	
— $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}$			
— $\text{NO} + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_2$			
— $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$			
Hampson, et al (1973) review	300	$< 1.1 \times 10^{-55} \text{ cm}^3 \text{ molecule}^{-3} \text{s}^{-1}$ where k is defined as: $-d[\text{NO}_2]/t = k[\text{NO}][\text{NO}_2][\text{H}_2\text{O}]^2$ main reaction probably is heterogeneous	± 0.7 estimate
— $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$			
Baulch, et al (1973) review	300	$\sim 2 \times 10^{-11}$	
Johnston (1966) review	300	8.3×10^{-12}	
*Harker, Johnston (1972) (D.G., D.D.D.)	300	8.7×10^{-12}	
— $\text{NO} + \text{NH}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}^*$			
Gehring, et al (1973)	300	Temperature effect is probably zero or very small. 8×10^{-12}	± 0.1
Reactions of NO with M to NH ₂			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
--- NO + H + M $\rightarrow$ HNO + M			
Baulch, et al (1973) review	230-700	$1.5 \times 10^{-32} \exp(300/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ M = H ₂	± 0.2
*This survey (DG)	220-400	$2.1 \times 10^{-32} \exp(300/T)$	± 0.2
Atkinson, Gvetanovic (1973)	286-390	$2.5 \times 10^{-32} \exp(270/T)$ M = H ₂	
Allen, Moorigat (1973)	180-300	$5.6(\pm 0.6) \times 10^{-33} \exp(+375(\pm 65)/T)$, M = Ar	
Thrush (1973) review	230-700	$2 \times 10^{-32} \exp(+300/T)$, M = H ₂	
--- NO + HO $\rightarrow$ NO ₂ + H			
Baulch, et al (1973) review	298-633	$5.2 \times 10^{-12} \exp(-15.1 \times 10^3/T)$ (a)	± 0.2 (298K)
		based on $k = 5.8 \times 10^{-10} \exp(-740/T)$ for reverse reaction (a) corrected expression	increasing to ± 0.3 (633K)
--- NO + HO(+M) $\rightarrow$ HNO ₂ (+M)			
Hampson, et al (1973a) review			
		Elevation/km	$k(T, M)$
	220	15	2.4×10^{-12}
	217	20	1.5×10^{-12}
	222	25	8.9×10^{-13}
	227	30	4.8×10^{-13}
	235	35	2.6×10^{-13}
	250	40	1.1×10^{-13}
	260	45	5.9×10^{-14}
Baulch, et al (1973) review	273-395	$2.2 \times 10^{-32} \exp(+1110/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ M=He	± 0.2 at 300K
			inc. to ± 0.3 at 395 K
	300	$2 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ (2d order high pressure limit)	± 0.3

Reactions of NO with H and HO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
— NO + HO ₂ → NO ₂ + OH			
* This survey (D.D.D.)	300	2 x 10 ⁻¹³	±0.5
Lloyd (1973) review	300	1.7 x 10 ⁻¹³ , E/R < 2000	±0.3
Payne, Stief, and Davis (1973)	300	3 x 10 ⁻¹³	±0.5 (a)
Simonaitis and Heicklen (1973)	300	> 1.5 x 10 ⁻¹³	±0.5 (a)
Baulch, et al (1973) review	300	3 x 10 ⁻¹³	±0.8
	(a) k/k(2HO ₂ → H ₂ O ₂) measured		
— NO + H ₂ → HNO + H			
Baulch, et al (1973) review	2000	5.3 x 10 ⁻¹⁸ cm ³ molecule ⁻¹ s ⁻¹	±0.2 (a)
	(a) No data. Value based on reverse rate		
— NO + H ₂ O → HNO + HO			
Baulch, et al (1973) review	2000	4 x 10 ⁻¹⁸	±0.2 (a)
	(a) No data. Value based on reverse rate. (Corrected)		
— NO + H ₂ O ₂ → HO + HNO ₂			
*Hampson, et al (1973) review	300	< 5 x 10 ⁻²⁰	
	500	~ 2 x 10 ⁻²⁰	
Gray, et al (1972)	300	< 5 x 10 ⁻²⁰	
— NO + CH ₃ (+M) → CH ₃ NO (+M)			
Glanzer, Troe (1973) review	295	1.7 x 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹ at high pressure see CH ₃ O + NO → . . .	±0.15
— NO + CH ₃ O → . . .			
— NO + CH ₃ O ₂ → CH ₃ O ₂ NO (a)			
→ CH ₂ O + HONO (b)			
→ CH ₃ O + NO ₂ (c)			
Demerjian, et al (1972) review (continued on next page)	300	k _c = 3.3 x 10 ⁻¹² exp(-500/T)	estimate

Reactions of NO with HO₂ to CH₃O₂

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
Heicklen (1973) review	298	$k_a/k = 0.6 \pm 0.1$ $k_b/k = 0.4 \pm 0.1$ $k_c/k < 0.02$ ($k = k_a + k_b + k_c$)	
NO ₂ + hv → NO + O			
Hampson, et al (1973a) review		λ/nm $\phi(\text{O}(^3\text{P}))$	
		295-398 1.0	
		400 0.70	
		405 0.29	
		410 0.12	
		420 0.02	
		440 0.001	
		absorption cross section data	
		108 < λ < 500 nm	
NO ₂ + M → NO + O + M		see reverse reaction	
NO ₂ + NO ₂ → NO + NO ₃			
Baulch, et al (1973) review		No recommendation	
NO ₂ + NO ₂ → NO + NO + O ₂			
Baulch, et al (1973) review	600-2000	$3.3 \times 10^{-12} \exp(-13540/T)$ $k_1[\text{NO}_2]^2 = -(1/2)d[\text{NO}_2]/dt$	± 0.15 (600-1000 K) increasing to 0.3 at 2000 K
NO ₂ + NO ₂ + M → N ₂ O ₄ + M			
Baulch, et al (1973) review	250-350	$4.7 \times 10^{-35} \exp(-680/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ M = N ₂	± 0.15 (a)
		(a) $k_f = k_r^K$ eq	

 Reactions of NO₂ with hv to NO₂

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of $\log k$
— $\text{N}_2\text{O}_4 + \text{M} \rightarrow \text{NO}_2 + \text{M}$			
Baulch, et al (1973) review	250-350	$4.2 \times 10^{-7} \exp(-5550/T)$	$\text{M} = \text{N}_2$ ± 0.15
Schofield (1973) review	250-350	$3.3 \times 10^{-7} \exp(-5540/T)$	$\text{M} = \text{N}_2$ ± 0.15
— $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO} (f)$			
— $\text{O}_2 + \text{NO} + \text{NO}_2 \rightarrow \text{NO}_2 + \text{NO}_3 (r)$			
*Baulch, et al (1973) review	300-850	$k_f = 2.3 \times 10^{-13} \exp(-1000/T)$	$\pm 0.4 (a)$
Johnston (1966) review	300-500	$k_r = k_f/K_{eq} = 8 \times 10^{-41} \exp(400/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$	± 0.4
	300-1100	$k_f = 3.8 \times 10^{-13} \exp(-2200/T)$	
		(a) Based on $\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$ and $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	
— $\text{NO}_2 + \text{NO}_3 (+\text{M}) \rightarrow \text{N}_2\text{O}_5 (+\text{M})$			
*This survey (HSJ)			
		Elevation/km $k (T, \text{M})$ $\log (M)$	
	220	$\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ 1.9×10^{-12}	18.60
	217	1.1×10^{-12}	18.27
	222	6.6×10^{-13}	17.93
	227	4.5×10^{-13}	17.59
	235	2.7×10^{-13}	17.26
	250	1.5×10^{-13}	16.92
	260	7.1×10^{-14}	16.60
— $\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} (f)$			
— $\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} (r)$			
Baulch, et al (1973) review	300	$k_f = 2.8 \times 10^{-30} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$	$\pm 0.3 (a)$
	300	$3.8 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	$\pm 0.4 (a)$
		(2d order high pressure limit)	

(continued on next page)

 Reactions of $\text{N}_2\text{O}_4 + \text{M}$ to $\text{NO}_2 + \text{NO}_3$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of $\log k$
— $\text{NO}_2 + \text{NH}_3 \rightarrow \text{NH}_2 + \text{HNO}_2$ Bedford, Thomas (1972)	300-340	$k_f = 2.2 \times 10^{-5} \exp(-9700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	± 0.3 (a)
— $\text{NO}_2 + \text{H} \rightarrow \text{HO} + \text{NO}$ *Hampson, et al (1973) review Baulch, et al (1973) review	273-300 615-660 300 298-633	$5.7 \times 10^{14} \exp(-10600/T) \text{ s}^{-1}$ (limiting first order expression) (a) $k_f = K_{\text{eq}} k_r$. $M = \text{N}_2\text{O}_5 + \text{NO}$ $6.7 \times 10^{-12} \exp(-13900/T)$ 4.8×10^{-11} $5.8 \times 10^{-10} \exp(-740/T)$	± 0.4 (a) ± 0.1 ± 0.2 at 298K increasing to ± 0.3 at 633K
— $\text{NO}_2 + \text{HO} (+M) \rightarrow \text{HNO}_3 (+M)$ *Tsang (1972) review Summarized in Hampson (1973a)	220 217 222 227 235 250 260	Elevation/km $k(T, M)$ 15 20 25 30 35 40 45 3.2×10^{-12} 2.5×10^{-12} 1.6×10^{-12} 8.5×10^{-13} 5.5×10^{-13} 2.7×10^{-13} 1.4×10^{-13}	± 0.3 Relative values from one elevation to another $\pm 5\%$ $M = \text{N}_2$
— $\text{NO}_2 + \text{HO} + M \rightarrow \text{HNO}_3 + M$ (f) — $\text{HNO}_3 + M \rightarrow \text{HO} + \text{NO}_2 + M$ (r) Baulch, et al (1973) review	273-400	$k_f = 3.6 \times 10^{-32} \exp(+1100/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	± 0.2
M = He (continued on next page)			
Reactions of NO_2 with NH_3 to HO			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of log k
$\text{NO}_2 + \text{HO}_2 \rightarrow \text{HNO}_2 + \text{O}_2$ Simonaitis, Heicklen (1973)	800-1200	$k_r = 2.7 \times 10^{-9} \exp(-15400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $M = \text{Ar}$	± 0.4
	300	$k_f = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2d order high pressure limit)	± 0.4
	298	$> 3 \times 10^{-13}$ $k/k(\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2) = 7 \pm 1$ (a) Interpretation of photolysis experiments, comparison with $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(a)
$\text{NO}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{O} + \text{NO}$ Glanzer, Troe (1973) review	300-1400	3.3×10^{-11} (a) Based on $k/k(\text{CH}_3 + \text{NO}) = 3.3$ at room temperature and on shock wave pyrolysis of CH_3NO_2	± 0.25 (a)
$\text{NO}_2 + \text{CH}_3 (+M) \rightarrow \text{CH}_3\text{NO}_2 (+M)$ Glanzer, Troe (1973) review	295	$2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (a) Based on high pressure limit rate ratio $k/k(\text{CH}_3 + \text{NO}) = 1.7$	± 0.1 (a)
$\text{NO}_2 + \text{CH}_3 + M \rightarrow \text{CH}_3\text{NO}_2 + M$ Glanzer, Troe (1973) review	900-1400	$6.9 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, $M = \text{Ar}$ (a) $k_f = k_f^{\text{eq}}$ see $\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \dots$	(a)
$\text{NO}_2 + \text{CH}_3\text{O} \rightarrow \dots$			

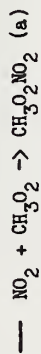
Reactions of NO_2 with HO_2 to CH_3O

Notes and
Reliability of
log k

Reaction Rate Constant
 $k/cm^3 \text{ molecule}^{-1} s^{-1}$

Temp.
Range/K

Reaction/Reference
* = Preferred Value



*Heicklen (1973) review

298

$k_a/k = 0.75 \pm 0.05$

$k_b/k = 0.25 \pm 0.1$

$k_c/k < 0.1$

Notes and
Reliability of
log k

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm molecule ⁻¹ s ⁻¹	
— NO ₃ + hv → NO + O ₂			
*Johnston (1972) review			
Very strong absorption spectrum 600-700nm. Pre-dissociated spectra. Alternative products (NO ₂ + O) energetically impossible at wave lengths above 576 nm. Destruction of NO ₃ observed; primary products not observed.			
Johnston (1973)			
— NO ₃ + M → NO ₂ + O + M			
— NO ₃ + NO ₃ → 2NO ₂ + O ₂			
*Johnston (1966) review			
*Baulch, et al (1973) review			
— NO ₃ + H ₂ O → HNO ₃ + HO			
Baulch, et al (1973) review			
— N ₂ + M → N + N + M			
*Baulch, et al (1973) review			
— N ₂ + HO → N ₂ O + H			
*Baulch, et al (1973) review			
Reactions of NO ₃ + hv to N ₂ + HO			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of $\log k$
$\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}$		. see reverse reaction	
$\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{HO}$			
Baulch, et al (1973) review	700-2500	$1.26 \times 10^{-10} \exp(-7600/T)$	± 0.2
Baldwin, et al (1973)	773	4.3×10^{-15}	± 0.15
$\text{N}_2\text{O} + \text{CO} \rightarrow \text{products}$			
Milks, Matula (1973)	1169-1655	$3.5 \times 10^{-13} \exp(-8650/T)$	
$\text{N}_2\text{O}_5 + \text{h}\nu \rightarrow \dots$			
* Jones, Wulf (1937)		λ/nm	Absn. cross sect./ $\text{cm}^2 \text{ molecule}^{-1}$, base e Scatter: 25%
		285	4.6×10^{-20} Reliability
		290	3.8×10^{-20} unknown
		300	2.3×10^{-20}
		310	1.2×10^{-20}
		320	0.69×10^{-20}
		330	0.39×10^{-20}
		340	0.24×10^{-20}
		350	0.17×10^{-20}
		360	0.095×10^{-20}
Holmes, Daniels (1934)		265	$18. \times 10^{-20}$
		280	8.3×10^{-20}
		>302	Zero
Murphy (1969)		$0.5 \times \phi(-\text{N}_2\text{O}_5) = \phi(0) = 0.31$	$\lambda = 280 \text{ nm}$
Hampson, et al (1973a) review		Meas. by Holmes, Daniels (1934) are consistent	
		Survey of photochemistry including data listed above	
Reactions of $\text{N}_2\text{O} + \text{M}$ to $\text{N}_2\text{O}_5 + \text{h}\nu$			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Elevation/km	k/s ⁻¹	Notes and Reliability of log k
$\text{N}_2\text{O}_5 (+M) \rightarrow \text{NO}_2 + \text{NO}_3 (+M)$ *This survey (HSJ)	220		15	5.0×10^{-7}	± 0.5
	217		20	1.8×10^{-7}	
	222		25	3.0×10^{-7}	
	227		30	5.5×10^{-7}	
	235		35	1.9×10^{-6}	
	250		40	1.6×10^{-5}	
	260		45	4.4×10^{-5}	
Extrapolated from data taken between 273 and 353 K.					
$\text{N}_2\text{O}_5 + M \rightarrow \text{NO}_2 + \text{NO}_3 + M$ $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ Hampson, et al (1973) review Morris, Niki (1973)	300		$k < 1 \times 10^{-20}$		see reverse reaction
	298		$< 1.3 \times 10^{-20}$		
$\text{NH}_2 + \text{H} + M \rightarrow \text{NH}_3 + M$ Baulch, et al (1973) review	2000-3000		$1.2 \times 10^{-33} \exp(11200/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, $M = \text{Ar}$	± 0.3 (a)	
			(a) $k_f = K_{\text{eq}} k_r$		
			see reverse reaction		
$\text{NH}_2 + \text{HO} \rightarrow \text{NH}_3 + \text{O}$ $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$ Baulch, et al (1973) review	800		$< 10^{-16}$	$k_f = K_{\text{eq}} k_r$	approximate
$\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{HO}$ Baulch, et al (1973) review			no data, no recommendation		
$\text{NH}_3 + M = \text{NH}_2 + \text{H} + M$ Baulch, et al (1973) review	2000-3000		$k = 1.5 \times 10^{-8} \exp(-42400/T) (M = \text{Ar})$		± 0.3 (a)
			(a) To be used when $P(M) < 4 \text{ atm.}$		
Reactions of $\text{N}_2\text{O}_5 + M$ to $\text{NH}_3 + M$					

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of $\log k$
--- $NH_3 + H \rightarrow NH_2 + H_2$			
Baulich, et al (1973) review	800	$< 10^{-16}$	approximate
--- $NH_3 + HO \rightarrow NH_2 + H_2O$			
Baulich, et al (1973) review		no recommendation. Data scatter badly	
Hack, Hoyermann (1973)	300	products may be $NH_2OH + H$ 2.8×10^{-13}	
Stuhl (1973a)	298	1.5×10^{-13}	± 0.1
Kurylo (1973)	298	4.1×10^{-14}	± 0.06
Smith (1973)	230-470	$2.3 \times 10^{-12} \exp(-800/T)$	

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of $\log k$
— $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} \text{ (f)}$			
— $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M} \text{ (r)}$			
Baulch, et al (1972) review	300	$k_f = 8.3 \times 10^{-33} \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $\text{M} = \text{H}_2$	± 0.2
	1700-5000	$= 1.8 \times 10^{-30} \text{ r}^{-1}$ $\text{M} = \text{Ar}$	± 0.3
		Rel. efficiencies: $\text{H}_2(1.0)$, $\text{Ar}(0.25)$	
		$-d[\text{H}]/dt = 2k[\text{H}]^2[\text{M}]$	
	2500-5000	$k_r = 3.7 \times 10^{-10} \exp(-48300/\text{T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$	± 0.3
		$\text{M} = \text{Ar}$	
		see reverse reaction	
— $\text{H} + \text{HO} \rightarrow \text{H}_2 + \text{O}$			
— $\text{H} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \text{ (f)}$			
— $\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{HO} + \text{M} \text{ (r)}$			
*Baulch, et al (1972) review	1000-3000	$k_f = 6.1 \times 10^{-26} \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $\text{M} = \text{N}_2$	± 0.3
	2000-6000	$k_r = 5.8 \times 10^{-9} \exp(-52900/\text{T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$	± 0.2
		$\text{M} = \text{N}_2$	
— $\text{H} + \text{HO}_2 \rightarrow \text{HO} + \text{HO} \text{ (1f)}$			
— $\text{HO} + \text{HO} \rightarrow \text{H} + \text{HO}_2 \text{ (1r)}$			
— $\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2 \text{ (2)}$			
— $\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O} \text{ (3)}$			
Baulch, et al (1972) review	290-800	$k_{1f} = 4.2 \times 10^{-10} \exp(-950/\text{T})$	$\pm 0.3 \text{ (a)}$
		$k_{1r} = k_{1f}/K_{\text{eq}} = 2.0 \times 10^{-11} \exp(-20200/\text{T})$	± 0.3
	290-800	$k_2 = 4.2 \times 10^{-11} \exp(-350/\text{T})$	± 0.4
		$k_{2r} = k_{2f}/K_{\text{eq}} = 9.1 \times 10^{-11} \exp(-29100/\text{T})$	± 0.4
		$k_3 = \text{no recommendation}$	
Lloyd (1973) review	300-1000	k_{1f} and k_2 - same as Baulch, et al	$> \pm 0.3 \text{ (a)}$
		$k_3 = 8.3 \times 10^{-11} \exp(-500/\text{T})$	$> \pm 0.5 \text{ (b)}$

(continued on next page)

Reactions of H with H to HO₂

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
Moortgat, Allen (1973)	297	$k_1 = 8.3 \times 10^{-12}$ $k_2 = 1 \times 10^{-11}$ $k_3 = 6.7 \times 10^{-12}$ (a) Reaction 1 and rate ratios control values for reactions 2 and 3. (b) Temperature coefficient estimated. (c) Secondary reaction in H + O ₂ + M systems, fit of concentration vs. time plots.	? (c) ? (c) ? (c)
--- H + H ₂ O → H ₂ + HO Baulch, et al (1972) review	300-2500	$1.5 \times 10^{-10} \exp(-10250/T)$	± 0.06 at 300K increasing to ± 0.2 at high temp.
--- H + H ₂ O ₂ → H ₂ + HO ₂ *Hampson, et al (1973) quoting Baulch, et al (1972) review	300-800	$2.8 \times 10^{-12} \exp(-1900/T)$	± 0.3
--- H + H ₂ O ₂ → H ₂ O + HO *Hampson, et al (1973) quoting Baulch, et al (1972) review		no recommendation	
--- H + HNO → H ₂ + NO Hampson, et al (1973) review	211-703	$> 5 \times 10^{-14}$	± 0.3
	2000	7×10^{-12}	± 0.3
Baulch, et al (1973) review	300	$10^{-13} < k < 10^{-12}$	
	2000	8×10^{-12}	± 0.2

Reactions of H with H₂O to HNO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Notes and Reliability of log k
— H + HNO ₂ → products			
Hampson, et al (1973) review		No data	
Baulch, et al (1973) review		No recommendation	
— H + HNO ₃ → products			
Hampson, et al (1973) review	300	$< 1 \times 10^{-13}$	estimate
Wayne (1973)	300	$< 1 \times 10^{-15}$	approximate upper limit
Baulch, et al (1973) review	300	$< 10^{-13}$	
— H + CH ₂ O → H ₂ + CHO			
Ridley, et al (1972)	297	5.4×10^{-14}	+0.04
Westenberg, de Haas (1972)	297-652	$2.2 \times 10^{-11} \exp(-1890/T)$	
— HO + M → H + O + M			
Baulch, et al (1972) review		no recommendation (E/R > 50000 K)	
— HO + HO → H + HO ₂		see reverse reaction	
— HO + HO → H ₂ + O ₂			
Baulch, et al (1972) review		no recommendation	
— HO + HO → H ₂ O + O (f)			
— O + H ₂ O → HO + HO (r)			
*Baulch, et al (1972) review			
Gardiner, et al (1973)	300-2000	$k_f = 1.0 \times 10^{-11} \exp(-550/T)$	+0.2
Westenberg, de Haas (1973a)	300-2000	$k_f = 1.1 \times 10^{-10} \exp(-9240/T)$	+0.2
— HO + HO + M → H ₂ O ₂ + M (f)	1200-2500	$k_f = 9.1 \times 10^{-11} \exp(-3500/T)$	
— H ₂ O ₂ + M → HO + HO + M (r)	300	$k_f = 2.3 \times 10^{-12}$	+0.06
Baulch, et al (1972) review	700-1500	$k_f = 2.5 \times 10^{-33} \exp(+2550/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	+0.1 700<T<950K
		$M = N_2; -d[\text{OH}]/dt = 2k[\text{OH}]^2[M]$	increasing to

(continued on next page)

Reactions of H with HNO₂ to HO with HO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
— $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$		$k_r = 2.0 \times 10^{-7} \exp(-22900/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, $M = \text{N}_2$; $k_f = k_r^{\text{eq}}$	± 0.3 at 1500K
Baulch, et al (1972) review		no recommendation	
Kaufman (1964) review	300	$k > 1 \times 10^{-11}$	estimate
Lloyd (1973) review	300-1000	$8.3 \times 10^{-11} \exp(-500/T)$	± 0.3
Hochanadel, et al (1972)	300	2×10^{-10}	
*This survey (H.S.J.)		The range of values $2 \times 10^{-11} < k < 2 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ should be considered in models of the stratosphere	
— $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}$		no recommendation	
Baulch, et al (1972) review			
— $\text{HO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$			
Baulch, et al (1972) review	300-2500	$3.6 \times 10^{-11} \exp(-2590/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	± 0.08 at 300 K ± 0.2 at high temp.
Wilson (1972) review	300-2000	$3.8 \times 10^{-11} \exp(-2600/T)$	± 0.3
Stuhl, Niki (1972)	298	7.1×10^{-15}	± 0.06
Westenberg (1973a)	298	7.6×10^{-15}	± 0.04
	352	1.8×10^{-14}	
	403	3.2×10^{-14}	
	518	1.4×10^{-13}	
	628	3.6×10^{-13}	
	745	6.6×10^{-13}	
Smith, Zellner (1973a)	210-460	$1.8 \times 10^{-11} \exp(-2330/T)$	(a)
(continued on next page)			
Reactions of HO with HO_2 and H_2			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
Paraskevopoulos (1973)	300	5.9 x 10 ⁻¹⁵	
Gardiner, et al (1973)	1200-2500	8.7 x 10 ⁻¹¹ exp(-3250/T)	
Greiner (1969)	300-500	6.8 x 10 ⁻¹² exp(-2020/T)	±0.15
— HO + H ₂ O → H ₂ O ₂ + H		(a) Reinterpretation by authors of reported data.	
Baulch, et al (1972) review		no recommendation	
— HO + H ₂ O ₂ → H ₂ O + HO ₂			
*Hampson (1973) quoting			
Baulch, et al (1972) review	300-800	1.7 x 10 ⁻¹¹ exp(-910/T)	±0.2
Gorse, Volman (1972)	300	k/k(HO + CO) = 8.13	
— HO + HNO → H ₂ O + NO			
Hampson, et al (1973) review	1600-2100	7 x 10 ⁻¹¹	±0.7
Baulch, et al (1973) review	2000	6 x 10 ⁻¹¹	±0.2
— HO + HNO ₂ → H ₂ O + NO ₂			
Demerjian, et al (1972) review	300	6.8 x 10 ⁻¹²	estimated, no data
Baulch, et al (1973) review	300	1.3 x 10 ⁻¹³	±0.6 estimated
— HO + HNO ₃ → H ₂ O + NO ₃			
Hampson, et al (1973) review	300-650	6 x 10 ⁻¹³ exp(-400/T)	±0.5
Johnston (1972) review	300-700	(1.5 to 2.0) x 10 ⁻¹³	±0.2
*This survey (H.S.J.)	220-270	1.3 x 10 ⁻¹³	
Wayne (1973)	300	1.5 x 10 ⁻¹³	approximate
Baulch, et al (1973) review	300	1.3 x 10 ⁻¹³	±0.3
Smith (1973)	300	8 x 10 ⁻¹⁴	

Reactions of HO with E₂O to HNO₃

Reaction/Reference * = Preferred Value	Temp. Range/k	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
HO + SO ₂ + M → HSO ₃ + M			
*Payne, Stief, Davis (1973)	300	2 x 10 ⁻³² cm ⁶ molecule ⁻² s ⁻¹ M = He	±0.3
Wayne (1973)	300	4.5 ± 1.5 x 10 ⁻³¹ M = Ar	
HO + HCl → H ₂ O + Cl			
Takacs, Glass (1973)	295	6.4 ± 1.5 x 10 ⁻¹³	±0.1
HO + CO → CO ₂ + H			
*This survey (D.G.)	200-400	1.4 x 10 ⁻¹³	±0.1 (a)
Wilson (1972) review	300-2000	5.1 x 10 ⁻¹³ exp(-300/T)	±0.3
Stuhl, Wink (1972)	300	1.35 x 10 ⁻¹³	±0.06
Westenberg, de Haas (1973a)	298	1.33 x 10 ⁻¹³	±0.04
	396	1.38 x 10 ⁻¹³	
	523	1.44 x 10 ⁻¹³	
	707	1.69 x 10 ⁻¹³	
	915	2.17 x 10 ⁻¹³	
Davis (1973)	220-370	2.05 x 10 ⁻¹³ exp(-75/T)	±0.04
Greiner (1969)	300-500	2.1 x 10 ⁻¹³ exp(-115/T)	±0.1
Smith and Zellner (1973)	300	1.45 x 10 ⁻¹³	(b)
Paraskevopoulos (1973)	300	1.43 x 10 ⁻¹³	
Peeters, Mahnen (1973)	1600-1900	4.7 x 10 ⁻¹³	
Gardiner, et al (1973)	1200-2500	6.7 x 10 ⁻¹² exp(-4000/T)	

(a) Small temperature coef. at low

temperatures. Ignore in models

(b) Data reported 210 < T < 460 K. Slight

positive temperature dependence,

possibly curved.

Reactions of HO with SO₂ to CO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of log k
--- $\text{HO} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{CHO}$			
*Morris, Niki (1971)	300	1.4×10^{-11}	± 0.1
Wilson (1972) review	300-1600	8×10^{-11}	± 1
Peeters, Mahnen (1973)	1400-1800	3.8×10^{-11}	
--- $\text{HO} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$			
Wilson (1972) review	300-2000	$4.7 \times 10^{-11} \exp(-2500/T)$	± 0.7
*Davis (1973) (D.G., R.H.)	240-370	$2.95 \times 10^{-12} \exp(-1770/T)$	± 0.04
Paraskevopoulos (1973)	300	8.3×10^{-15}	
Peeters, Mahnen (1973)	1100-1900	$5 \times 10^{-11} \exp(-3000/T)$	
Greiner (1970)	300-500	$5.5 \times 10^{-12} \exp(-1900/T)$	± 0.1
--- $\text{HO} + \text{C}_2\text{H}_2 \rightarrow \text{products}$			
Smith and Zellner (1973)	210-460	$2.0 \times 10^{-12} \exp(-250/T)$	
Pastrana, Carr (1973)	300	1.47×10^{-13}	(a)
--- $\text{HO} + \text{C}_2\text{H}_4 \rightarrow \text{products}$			
Stuhl (1973c)	298	3×10^{-12}	± 0.12
Smith and Zellner (1973)	210-460	$7.5 \times 10^{-12} \exp(-110/T)$	
--- $\text{HO} + \text{C}_2\text{H}_6 \rightarrow \text{products}$			
Paraskevopoulos (1973)	300	3.0×10^{-13}	
--- $\text{HO} + \text{C}_3\text{H}_6 \rightarrow \text{products}$			
Stuhl (1973c)	298	1.45×10^{-11}	± 0.05
--- $\text{HO} + \text{C}_4\text{H}_{10} \rightarrow \text{products}$			
* Stuhl (1973b)		2.35×10^{-12}	± 0.06

Reactions of HO with CH_2O to C_4H_{10}

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
$\text{HO}_2 + \text{M} \rightarrow \text{H} + \text{O}_2 + \text{M}$ Baulch, et al (1972) review Lloyd (1973) review	300-2000	$3.5 \times 10^{-9} \exp(-23000/\text{T})$, M = Ar same recommendation (a) $k_f = k_r^{\text{K}} \text{eq}$	± 0.2 (a)
$\text{HO}_2 + \text{M} \rightarrow \text{HO} + \text{O} + \text{M}$ Baulch, et al (1972) review		no recommendation	
$\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$ Baulch, et al (1972) review Lloyd (1973) review	300-800 300-1000	$1.2 \times 10^{-12} \exp(-9400/\text{T})$ same recommendation. $k_f = k_r^{\text{K}} \text{eq}$	± 0.3
$\text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{HO}$ Baulch, et al (1972) review Lloyd (1973) review	300-800 300-1000	$4.7 \times 10^{-11} \exp(-16,500/\text{T})$ same recommendation $k_f = k_r^{\text{K}} \text{eq}$	± 0.2
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ *Hampson (1973) review Baulch, et al (1972) review Lloyd (1973) review	300-1000 300 300-1000	$3 \times 10^{-11} \exp(-500/\text{T})$ cm ³ molecule ⁻¹ s ⁻¹ 3.3×10^{-12} $1.7 \times 10^{-11} \exp(-500/\text{T})$ $-\text{d}[\text{HO}_2]/\text{dt} = 2k[\text{HO}_2]^2$. Temperature coefficient estimated	± 0.3 at 300 K ± 0.3 at 300 K larger at higher T
$\text{HO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{HO}$ *Payne, Stief, Davis (1973)	300	9×10^{-16} cm ³ molecule ⁻¹ s ⁻¹ (relative rate measurement - reference reaction: $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$)	± 0.3

Reactions of HO₂ with M to SO₂

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Notes and Reliability of log k
— HO ₂ + CO → CO ₂ + HO			
*This survey (D.D.D., H.I.S.)			
Lloyd (1973) eval.	300	<10 ⁻¹⁹	a
Westenberg, de Haas (1972)	300-1000	1.7 x 10 ⁻¹³ exp(-5000/T)	b
Davis, Payne, Stief (1972)	300	-1 x 10 ⁻¹²	c,d
Wyrsh, et al (1973)	300	<10 ⁻²⁰	e
Simonaitis, Heickeln (1973)	300	<3 x 10 ⁻¹⁸	
Volman, Gorse (1972)	373-473	<5 x 10 ⁻¹⁸	e
Baldwin, Walker, Webster (1970)	330	<10 ⁻¹⁵	f
Vardanyan, Dangyan,	713-773	1 x 10 ⁻¹⁰ exp (-11500/T)	e
Sachyan (1972)	878-952	2.2 x 10 ⁻¹⁰ exp (-11500/T)	
NOTE: a. The low value of k selected in this evaluation is based on the evaluation by Lloyd and the measurements by Davis, Payne, Stief and Simonaitis, Heicklen.			
b. Based on Davis, Payne and Stief (1972) and high T results. Temperature coef. probably maximum value.			
c. Indirect measurement using a low-pressure discharge flow system.			
d. Relative rate measurement - reference reaction: H + HO ₂ → HO + HO			
e. Relative rate measurement - reference reaction: HO ₂ + HO ₂ → H ₂ O ₂ + O ₂			
f. Relative rate measurement - reference reaction: HO + CO → CO ₂ + H			
— HO ₂ + CH ₂ O → H ₂ O ₂ + CHO			
*Lloyd (1973) review	200-1000	1.7 x 10 ⁻¹² exp (-4000/T)	>+1 at 300K, ±0.2 at 800K
Baldwin, et al (1972)	773	1.6 x 10 ⁻¹⁵	(a)
(note on next page)			
Reactions of HO ₂ with CO and CH ₂ O			

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $\text{k/cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of log k
— $\text{HO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$ Demerjian et al (1972) review	300	$\text{k}(\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2) = 3.0 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ 6.7×10^{-14}	(a) Derived by computer fit to data. Based on estimate
— $\text{HO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{O} + \text{HO} ?$ Walker (1973)	773	2.5×10^{-17}	(a)
— $\text{HO}_2 + \text{C}_2\text{H}_4 \rightarrow$ addition products Lloyd (1973) review	300	(a) Relative to k ($\text{HO}_2 + \text{HCHO} = 1.6 \times 10^{-15}$) -1.7×10^{-17}	$> \pm 1$ (a)
— $\text{HO}_2 + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O}_2 + \text{C}_2\text{H}_5$ Lloyd (1973) review	300-1000	$-1.7 \times 10^{-12} \exp(-7000/T)$	± 1 (a)
— $\text{HO}_2 + \text{C}_3\text{H}_8 \rightarrow \text{H}_2\text{O}_2 + \text{i-C}_3\text{H}_7$ Lloyd (1973) review	300-1000	(a) Relative rate data versus $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ and $\text{HO}_2 + \text{CO} \rightarrow \text{HO} + \text{CO}_2$. Temp. coef. estimated. $< 3.3 \times 10^{-13} \exp(-5300/T)$	± 1 (a)
— $\text{HO}_2 + \text{n-C}_4\text{H}_{10} \rightarrow \text{H}_2\text{O}_2 + \text{s-C}_4\text{H}_9$ (primarily) Lloyd (1973) review	300-1000	(a) Based on upper limit meas. Temp. coef. estimated. $8.3 \times 10^{-13} \exp(-5300/T)$	± 1 (a)

Reactions of HO_2 with CH_3O_2 to $\text{n-C}_4\text{H}_{10}$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Notes and Reliability of $\log k$
— $\text{HO}_2 + \text{i-C}_4\text{H}_{10} \rightarrow \text{H}_2\text{O}_2 + \text{t-C}_4\text{H}_9$ Lloyd (1973) review	300-1000	$1.7 \times 10^{-13} \exp(-3500/T)$	± 1 (a)
— $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$		(a) Based on upper limit meas. Temp. coef. estimated.	
— $\text{H}_2\text{O}_2 + h\nu \rightarrow \text{HO} + \text{HO}$ *Hampson (1973) review		see reverse reaction	
Absorption coefficient (cross section)			
	λ/nm	$\sigma/\text{cm}^2 \text{molecule}^{-1}$, base e	
	190	80×10^{-20}	
	195	60×10^{-20}	
	200	54×10^{-20}	
	205	46×10^{-20}	
	210	40×10^{-20}	
	215	34×10^{-20}	
	220	28×10^{-20}	
	225	24×10^{-20}	
	254	7.4×10^{-20}	
Quantum yields (primary)			
	$\phi(-\text{H}_2\text{O}_2) = 1.0 \lambda > 200\text{nm}$.		
See ref. for other, minor, channels pertinent for $\lambda < 200\text{nm}$.			
	see reverse equation		
— $\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{HO} + \text{HO} + \text{M}$			
— $\text{HNO} + \text{M} \rightarrow \text{H} + \text{NO} + \text{M}$ *Baulch, et al (1973) review	230-700	$5 \times 10^{-8} \exp(-24,500/T) \text{ M} = \text{H}_2$	± 0.2 (a)
(a) No data. Value based on reverse rate			

Reactions of HO_2 with $\text{i-C}_4\text{H}_{10}$ to $\text{HNO} + \text{M}$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 \text{ molecule}^{-1} s^{-1}$	Notes and Reliability of log k
— $HNO + HNO \rightarrow H_2O + N_2O$			
*Baulch, et al (1973) review	300	4×10^{-15}	± 0.3
— $HNO_2 + h\nu \rightarrow HO + NO$			
Johnston (1973)		$6.45 \times 10^{-4} s^{-1}$ (Daylight)	
— $HNO_3 + h\nu \rightarrow HO + NO_2$		absorption: 300–400nm	
*Johnston, (1972) review		Elevation/km $k(\text{noon})/s^{-1}$	
	220	15 5.1×10^{-7}	± 0.15
	217	20 7.7×10^{-7}	Rates are for
	222	25 2.8×10^{-6}	45° latitude,
	227	30 1.4×10^{-5}	solar equinox
	235	35 4.1×10^{-5}	standard ozone
	250	40 7.6×10^{-5}	background
	260	45 1.1×10^{-4}	
*Hampson, et al (1973) review		Absorption coefficients. See also Text.	
Johnston, Chang (1973)		$\phi = 1 \quad 200 < \lambda < 315nm$	(a)
— $HNO_3 + M \rightarrow HO + NO_2 + M$		(a) Products probably those shown above.	
— $SO + SO \rightarrow SO_2 + S$		see reverse reaction	
*Schofield (1973) review (WHB)			
	300	$< 3 \times 10^{-15}$	
	1000	$< 2 \times 10^{-13}$	
		only upper limit estimates are available	
— $SO_2 + CH_3 (+M) \rightarrow CH_3SO_2 (+M)$			
James, et al (1973)	300	$3 \times 10^{-13} cm^3 \text{ molecule}^{-1} s^{-1}$	± 0.1

Reactions of $HNO + HNO$ to $SO_2 + CH_3$

Notes and
Reliability of
log k

 Reaction Rate Constant
k/cm³ molecule⁻¹ s⁻¹

 Temp.
Range/K

 Reaction/Reference
* = Preferred Value

— Cl + OClO → 2ClO

Watson (1973) review

 5.9 ± 0.9 × 10⁻¹¹

±0.1

(E = 0 ± 1 kJ/mol)

 — Cl + CH₄ → HCl + CH₃

Davis, et al (1970)

 1.5 ± 0.1 × 10⁻¹³

Pettis, Knox (1964)

 4 × 10⁻¹¹ exp(-1930/T)

Clyne, Walker (1973)

 5.1 × 10⁻¹¹ exp(-1790/T)

 — CO + CH₃O → . . .

 see CH₃O + CO

 — CH₂O + hv → CHO + H (a)

 → CO + H₂ (b)

*Calvert, et al. (1972) (D.C.)

 ϕ_a + ϕ_b = 1, 290 < λ < 360 nm

λ/nm	ϕ _a	ϕ _b	absn. cross section cm ² molecule ⁻¹ base e**
290	0.81	0.19	31.8 × 10 ⁻²¹
300	0.66	0.34	32.5
310	0.52	0.48	31.4
320	0.40	0.60	23.4
330	0.29	0.71	23.6
340	0.18	0.82	19.7
350	0.09	0.91	8.37
360	0.01	0.99	1.77

**Averaged for 10 nm bands. See McQuigg, Calvert

 (1969) for graph of absn. coefficient vs. wave
length.

(continued on next page)

 Reactions of Cl + OClO to CH₂O + hv

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Notes and Reliability of $\log k$
Sperling, Toby (1973)			
--- $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$ (1)		λ/nm	
--- $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}$ (2a)		ϕ_a	
$\rightarrow \text{CH}_2\text{O} + \text{HNO}$ (2b)		ϕ_b	
--- $\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$ (3a)		313 0.8 0.2	
$\rightarrow \text{CH}_2\text{O} + \text{HNO}_2$ (3b)		334 0.45 0.25	
--- $\text{CH}_3\text{O} + \text{CO} \rightarrow \text{products}$ (4)		366 0.2 0.45	
Demerjian, et al (1972) review	300	$k_1 = 1.6 \times 10^{-17}$ $\sim 4.2 \times 10^{-13} \exp(-3000/T)$	
adjusted to fit $\text{C}_4\text{H}_{10}/\text{NO}_x$ simulation studies			
		$k_{2a} = 1.7 \times 10^{-13}$	
		$k_{2b}/k_{2a} = 0.17$	
		$k_{3b} = 3.3 \times 10^{-13}$	
		$k_{3b}/k_{3a} = 0.1$	
		$k_1 = 3 \times 10^{-18}$	
*Heicklen (1973)	298	$\sim 1.6 \times 10^{-13} \exp(-3300/T)$	
		$k_2 = 8 \times 10^{-14}$	
	298	$k_1/k_2 = 4.7 \times 10^{-5} \pm 20\%$	ratio probably is smaller at -20 K
		$k_{2b}/k_2 = 0.145 \pm 0.015$	
		$k_2/k_3 = 1.2 \pm 0.1$	
(continued on next page)			
Reactions of CH_3O			

Reactions of CH_3O_2

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4.2.1 Introduction

The rate constants are all listed for the exothermic reaction path. The form of the rate constants listed in the following table have been fitted to experimental data where available and either use a theoretical temperature dependence for extrapolation, or the general trend of the data itself has been used to suggest the temperature dependence. The table provided here was prepared in December 1973.

4.2.2 VIBRATIONAL ENERGY TRANSFER PROCESSES

(R. L. Taylor, December 1973)

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant-cm ³ molecule ⁻¹ s ⁻¹
1	CO ₂ (010) + M → CO ₂ (000) + M Taylor and Bitterman (1969); Simpson et al (1969); Simpson and Chandler (1970); Buchwald and Bauer (1972); Sato and Tsuchiya (1972) Taylor and Bitterman (1969); Buchwald and Bauer (1972)	200 < T < 2000	M = CO ₂ k = 4.64 x 10 ⁻¹⁰ exp(-76.75/T ^{1/3}) M = N ₂ , O ₂ k = 6.69 x 10 ⁻¹⁰ exp(-84.07/T ^{1/3}) M = H ₂ O k = 3.22 x 10 ⁻¹³ exp (22.91/T ^{1/3})
2	N ₂ (v = 1) + M → N ₂ (v = 0) + M Millikan and White (1963); Taylor and Bitterman (1969); Kovacs and Mack (1972) Taylor and Bitterman (1969); vonRosenberg et al (1972); Evans (1972)	1000 < T < 5000 200 < T < 2000	M = N ₂ , O ₂ , CO ₂ k = 8.53x10 ⁻⁷ exp(-273.10/T ^{1/3}) M = H ₂ O k = 1.07 x 10 ⁻¹⁰ exp (-69.90/T ^{1/3})
3	H ₂ O (010) + M → H ₂ O (000) + M Taylor and Bitterman (1969) Corrected by 0.1 Bauer (1968); Monk, (1969); Henderson et al (1969) Monk (1969)	200 < T < 600 200 < T < 400	M = H ₂ O k = 1.0x10 ⁻¹¹ + 2.68x10 ⁻⁸ exp(-70.00/T ^{1/3}) M = N ₂ , CO ₂ · k = 5.37 x 10 ⁻¹⁰ exp (-70.00/T ^{1/3}) M = O ₂ (see process (9))
4	O ₂ (v = 1) + M → O ₂ (v = 0) + M Millikan and White (1963); Taylor and Bitterman (1969); Kovacs and Mack (1972) Taylor and Bitterman (1969)	200 < T < 5000	M = N ₂ , O ₂ , CO ₂ k = 4.81 x 10 ⁻⁸ exp(-169.60/T ^{1/3}) M = H ₂ O k ≤ 3.60 x 10 ⁻¹⁰ exp(-60.69/T ^{1/3})
5	CO ₂ (001) + N ₂ (v = 0) → CO ₂ (000) + N ₂ (v = 1) Rosser et al (1969); Taylor and Bitterman (1969); Margottin-Maclou et al (1971); Sato and Tsuchiya (1972)	200 < T < 2000	k = 1.71 x 10 ⁻⁶ exp (-175.30/T ^{1/3}) + 6.07 x 10 ⁻¹⁴ exp (15.27/T ^{1/3})

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant-cm ³ molecule ⁻¹ s ⁻¹
6	$\text{H}_2\text{O} (010) + \text{O}_2 (v=0) \rightarrow \text{H}_2\text{O} (000) + \text{O}_2 (v=1)$ Taylor and Bitterman (1969)	200 < T < 400	$k = 1.00 \times 10^{-12}$
7	$\text{N}_2 (v=1) + \text{O}_2 (v=0) \rightarrow \text{N}_2 (v=0) + \text{O}_2 (v=1)$ Taylor and Bitterman (1969); Breshears and Bird (1968)	200 < T < 5000	$k = 1.74 \times 10^{-10} \exp(-124.00/T^{1/3})$
8	$\text{O}_2 (v=1) + \text{CO}_2 (000) \rightarrow \text{O}_2 (v=0) + \text{CO}_2 (010)$	200 < T < 400	$k = 1.78 \times 10^{-12} \exp(-37.94/T^{1/3})$
9	$\text{CO}_2 (100) + \text{M} \rightarrow \text{CO}_2 (020) + \text{M}$ Taylor and Bitterman (1969); Sharma (1968); Moore (1973)	200 < T < 400	$\text{M} = \text{N}_2, \text{O}_2 \quad k \geq 3.0 \times 10^{-11}$
10	$\text{CO}_2 (001) + \text{M} \rightarrow \text{CO}_2 (030) + \text{M}$ Taylor and Bitterman (1969); Rosser et al (1969); Stephenson and Moore, (1972); Sato and Tsuchiya (1972); Taylor and Bitterman (1969); Rosser and Gerry (1969); Stephenson and Moore (1972); Taylor and Bitterman (1969); Rosser and Gerry (1971); Sato and Tsuchiya (1972); Seery (1972 a); Rosser et al (1971); Sato and Tsuchiya (1972); Stephenson and Moore (1972); Taylor and Bitterman (1969); Rosser and Gerry (1969); Heller and Moore (1970)	200 < T < 2000	$\text{M} = \text{N}_2 \quad k = 1.00 \times 10^{-15} + 5.16 \times 10^{-11} \exp(-76.75/T^{1/3})$ $\text{M} = \text{O}_2 \quad k = 1.10 \times 10^{-15} + 7.31 \times 10^{-11} \exp(-76.75/T^{1/3})$ $\text{M} = \text{CO}_2 \quad k = 3.0 \times 10^{-15} + 1.72 \times 10^{-10} \exp(-76.75/T^{1/3})$ $\text{M} = \text{CO} \quad k = 2.20 \times 10^{-15} + 9.69 \times 10^{-11} \exp(-76.75/T^{1/3})$ $\text{M} = \text{H}_2\text{O} \quad k = 4.0 \times 10^{-13}$
11	$\text{H}_2\text{O} (100) + \text{M} \rightarrow \text{H}_2\text{O} (020) + \text{M}$ Sarjeant et al (1972); Center and Kung (1973); Mechanism is author's prejudice	200 < T < 1000 4000 < T < 2000	$\text{M} = \text{H}_2\text{O} \quad k = 2.50 \times 10^{-12} \text{ T}^{0.5}$ $\text{M} = \text{N}_2, \text{O}_2, \text{CO}_2 \quad k \approx 1.0 \times 10^{-14} \text{ T}^{0.5}$
12	$\text{CO} (v=1) + \text{M} \rightarrow \text{CO} (v=0) + \text{M}$ Millikan and White (1963); Kovacs and Mack (1972); vonRosenberg et al (1971)	200 < T < 5000 1000 < T < 3000	$\text{M} = \text{CO}, \text{N}_2, \text{O}_2 \quad k = 6.67 \times 10^{-8} \exp(-208.30/T^{1/3})$ $\text{M} = \text{H}_2\text{O} \quad k = 3.12 \times 10^{-10} \exp(-64.99/T^{1/3})$

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant - $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
13	$\text{N}_2 (v=1) + \text{CO} \rightarrow \text{N}_2 (v=0) + \text{CO} (v=1)$ Sato et al (1969); vonRosenberg et al (1972); McLaren and Appleton (1971); Zittel and Moore (1972)	$200 < T < 2000$	$k = 1.78 \times 10^{-6} \exp(-209.90/T^{1/3}) + 6.98 \times 10^{-13} \exp(-25.60/T^{1/3})$
14	$\text{CO} (v=1) + \text{O}_2 (v=0) \rightarrow \text{CO} (v=0) + \text{O}_2 (v=1)$ Sato et al (1969); Center (1973)	$1000 < T < 3000$	$k = 3.50 \times 10^{-10} \exp(-124.00/T^{1/3})$
15	$\text{CO}_2 (001) + \text{CO} (v=0) \rightarrow \text{CO}_2 (000) + \text{CO} (v=1)$ Rosser et al (1971); Seery (1972); Stephenson and Moore (1972); Borrell and Millward (1972); Buchwald and Bauer (1972); Sato and Tsuchiya (1972)	$1000 < T < 3000$	$k = 1.56 \times 10^{-11} \exp(-30.12/T^{1/3})$
16	$\text{CO} (v=1) + \text{H}_2\text{O} (000) \rightarrow \text{CO} (v=0) + \text{H}_2\text{O} (000)$		Data can be interpreted as either V-T or V-V process. See process (12) for V-T interpretation.
17	$\text{NO} (v=1) + \text{M} \rightarrow \text{NO} (v=0) + \text{M}$ Basco et al (1961); Taylor (1973) Robbins (1959); Bauer (1959); Basco et al (1961); Wray (1962); Kneser et al (1967); Breshears and Bird (1969); Bradley and Lewis (1969); Hochenade and Ghormley (1969); Kamimoto and Matsui (1970); Billingsley and Callear (1969); Billingsley and Callear (1971); Green and Hancock (1973); Stephenson (1973) Basco et al (1961) Basco et al (1961) Basco et al (1961); Taylor et al (1967)	$200 < T < 2000$	$M = \text{N}_2, \text{O}_2 \quad k = 6.75 \times 10^{-7} \exp(-182.83/T^{1/3})$ $M = \text{NO} \quad k = 2.49 \times 10^{-11} \exp(-40.19/T^{1/3})$
18	$\text{N}_2 (v=1) + \text{NO} (v=0) \rightarrow \text{N}_2 (v=0) + \text{NO} (v=1)$ Taylor et al (1967); Basco et al (1961); Callear (1962)	$200 < T < 2000$	$M = \text{CO}_2 \quad k = 1.66 \times 10^{-11} \exp(-40.19/T^{1/3})$ $M = \text{H}_2\text{O} \quad k = 7.47 \times 10^{-10} \exp(-40.19/T^{1/3})$ $M = \text{CO} \quad k = 2.49 \times 10^{-12} \exp(-40.19/T^{1/3})$ $k = 4.22 \times 10^{-10} \exp(-86.35/T^{1/3})$

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant - $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
19	$\text{CO} (v=1) + \text{NO} (v=0) \rightarrow \text{CO} (v=0) + \text{NO} (v=1)$ Basco et al (1961); Callear (1965); Taylor et al (1967)	$200 < T < 2000$	$k = 3.58 \times 10^{-11} \exp(-49.93/T^{1/3})$ $+ 1.26 \times 10^{-8} \exp(-115.13/T^{1/3})$
20	$\text{N}_2 (v=1) + \text{N}_2\text{O} (000) \rightarrow \text{N}_2 (v=0) + \text{N}_2\text{O} (001)$ Roach and Smith (1969); Yardley (1968); McNeal et al (1972); Stephenson and Moore (1972).	$200 < T < 2000$	$k = 5.4 \times 10^{-14} \exp(10.2/T^{1/3})$
21	$\text{OH} (v=1) + \text{M} \rightarrow \text{OH} (v=0) + \text{M}$ Worley et al (1971, 1972) Values are derived from the reported values for OH ($v=9$)	$T = 300$	$M = \text{O}_2 \quad k(1) = 1 \times 10^{-15}$ $= \text{N}_2 \quad = 3.6 \times 10^{-16}$ $= \text{NO} \quad = 1.5 \times 10^{-14}$ $= \text{N}_2\text{O} \quad = 4.8 \times 10^{-15}$ $= \text{CO}_2 \quad = 2.4 \times 10^{-15}$ $= \text{H}_2\text{O} \quad = 2.0 \times 10^{-14}$
22	$\text{N}_2 (v=1) + \text{O} \rightarrow \text{N}_2 (v=0) + \text{O}$ Breshears and Bird (1968); McNeal et al (1972)	$200 < T < 3000$	$k = 1.07 \times 10^{-10} \exp(-69.90/T^{1/3})$
23	$\text{O}_2 (v=1) + \text{O} \rightarrow \text{O}_2 (v=0) + \text{O}$ Kiefer and Lutz (1967)	$200 < T < 2000$	$k = 6.88 \times 10^{-9} \exp(-76.75/T^{1/3})$
24	$\text{CO} (v=1) + \text{O} \rightarrow \text{CO} (v=0) + \text{O}$ Center (1973)	$200 < T < 3000$	$k = 9.9 \times 10^{-8} \exp(-118.07/T^{1/3})$
25	$\text{CO}_2 (010) + \text{O} \rightarrow \text{CO}_2 (000) + \text{O}$ Center (1973a)	$200 < T < 3000$	$k = 2.32 \times 10^{-9} \exp(-76.75/T^{1/3})$
26	$\text{O}_3 (100) + \text{M} \rightarrow \text{O}_3 (001) + \text{M}$ Rosen and Cool (1973)	300	$M = \text{N}_2, \text{O}_2, \text{O}_3, \text{CO}_2 \quad k \geq 4.9 \times 10^{-12}$ Note: Data refers to $k_{26} + k_{27}$
27	$\text{O}_3 (100) + \text{O}_3 (001) \rightarrow \text{O}_3 (101) + \text{M}$ Rosen and Cool (1973)	300	See Above

No.	Reaction/Reference	Temp. Range/ $^{\circ}\text{K}$	Reaction Rate Constant- $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
28	$\text{O}_3(100) + \text{M} \rightarrow \text{O}_3(000) + \text{M}$	300	$\text{M} = \text{N}_2 \quad k = 2.4 \times 10^{-14}$ Note: Data refer to $k_{28} + k_{29}$ $\text{M} = \text{O}_2 \quad k = 2.9 \times 10^{-14}$ $\text{M} = \text{O}_3 \quad k = 1.1 \times 10^{-13}$ $\text{M} = \text{CO}_2 \quad k = 1.9 \times 10^{-13}$
29	$\text{O}_3(001) + \text{M} \rightarrow \text{O}_3(000) + \text{M}$	300	See Above
30	$\text{O}_3(100) + \text{M} \rightarrow \text{O}_3(010) + \text{M}$	300	Possible alternate mechanism for (28) + (29). See text.
31	$\text{O}_3(001) + \text{M} \rightarrow \text{O}_3(010) + \text{M}$		
32	$\text{O}_3(010) + \text{M} \rightarrow \text{O}_3(000) + \text{M}$		
33	$\text{O}_3(010) + \text{CO}_2(000) \rightarrow \text{O}_3(000) + \text{CO}_2(010)$		
34	$\text{CO}_2(001) + \text{O}_3(000) \rightarrow \text{CO}_2(100) + \text{O}_3(100)$ Cool and Airey, (1973); vonRosenberg and Lowenstein (1973); Rosen and Cool (1973)	300	$k = 7.6 - 12 \times 10^{-13}$

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4.3 High Temperature Air Reactions (R. L. Taylor)

No.	Reaction	Temp. Range/K	Reaction Rate Constant, cm ³ /molecule-sec	References
(1)	$O + O + M \rightarrow O_2 + M$	2000 < T < 10,000	$M = N_2, k = 1.7 \times 10^{-32} T^{-1/2}$ $M = O_2, k = 2.2 \times 10^{-28} T^{-3/2}$ $M = O, k = 6.2 \times 10^{-28} T^{-3/2}$ $M = N, NO, k = 8.3 \times 10^{-33} T^{-1/2}$	Lin + Teare (63) Wray (62)
(2)	$N + N + M \rightarrow N_2 + M$	2000 < T < 10,000	$M = N_2, k = 7.6 \times 10^{-32} T^{-1/2}$ $M = O_2, O, NO, k = 3.0 \times 10^{-32} T^{-1/2}$ $M = N, k = 6.5 \times 10^{-27} T^{-3/2}$	Lin + Teare (63) Wray (62)
(3)	$N + O + M \rightarrow NO + M$	2000 < T < 10,000	$M = N_2, O_2, N, O, k = 2.8 \times 10^{-28} T^{-3/2}$ $M = NO, k = 5.5 \times 10^{-27} T^{-3/2}$ $k = 2.7 \times 10^{-11}$	Lin + Teare (63) Wray (62)
(4)	$N + NO \rightarrow N_2 + O$	2000 < T < 10,000		Wray (62), Liu + Teare (63) Baulch et al (69)
(5)	$N + O_2 \rightarrow NO + O$	2000 < T < 10,000	$k = 2.2 \times 10^{-14} T \exp(-3560/T)$	Wray (62), Lin + Teare (63) Baulch et al (69)
(6)	$NO + NO \rightarrow N_2O + O$	2000 < T < 10,000	$k = 0.4 T^{-5/2} \exp(-43,000/T)$	Camac + Feinberg (67)

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4.4 Ion Molecule Reactions (E. E. Ferguson)

4.4.1 Explanation of Tables

The reactions are listed in the order: (1) atomic ions reacting with neutrals, (2) molecular ions reacting with neutrals. The ions are listed according to atomic number except that obviously related reactions may be grouped. No distinction is made between ion-atom interchange and charge-transfer reactions, i.e. those in which heavy particles are transferred as contrasted to electrons. The rate constant is defined as the coefficient k in the expression $-d[A^+]/dt = k[A^+][B]$ where $[A^+]$ and $[B]$ are the ion and neutral concentrations in the reaction $A^+ + B \rightarrow$ products.

The entries in the Tables are:

k : Rate constant in $\text{cm}^3 \text{ sec}^{-1}$ (molecule⁻¹ implied)

Uncertainty: See Introduction for Discussion

Method : Indicated by the following abbreviations

FA Flowing Afterglow

This is a relatively high pressure experiment with many reactant ion collisions prior to reaction so that the reactants are almost always known to be in their ground states. This method has the greatest chemical versatility of all of the methods and so has produced a large fraction of the available data. FA data have been obtained in the temperature range 80 - 600 K.

SA Stationary Afterglow

This is a high pressure experiment in which reactant ions can safely be assumed to be in their ground states in most cases. The ionizing discharge may however produce excited or dissociated neutral reactants. Photoionization sources have alleviated this problem but have been very limited in their chemical versatility. Some SA experiments have covered a range of gas temperatures from about 180 - 600 K.

DT Drift Tube

This technique has only recently been applied to ion-molecule reactions with good results. The reactants are expected to be in their ground states. The method has the advantage of yielding reaction rate constants for ion translational energy going from thermal up into the several electron volt range. The data on energy dependences thus tends to augment thermal energy data in many cases.

MS Mass Spectrometer Ion Source

Most MS data in the literature have been obtained at low pressure (thin target conditions) and this raises the possibility that the ions may have been produced in excited states which can be quite misleading. Some MS experiments, particularly those of Kebarle have worked at relatively high pressure and have thereby avoided this problem. Low

pressure mass spectrometer ion sources measure reaction cross sections rather than reaction rate constants. Since most applications require rate constants this introduces a small uncertainty. Essentially

$\int \sigma(E) E^{\frac{1}{2}} dE$ must be approximated by $\bar{\sigma}(E) \bar{E}^{\frac{1}{2}}$, while in rate constant measuring experiments (FA, SA, DT) the experiment itself accomplishes the integration. The low pressure MS experiments also involve a small electric field in the ion sampling so that the cross sections are measured somewhat above thermal energy.

B Beam

Beam data are always obtained at energies in excess of thermal. The extrapolations to low energy introduces some uncertainty into the low energy cross sections. This is more serious for ion-atom interchange reactions than for charge-transfer reactions in most cases. The beam technique has been a very versatile technique in the kinds of neutral reactants which can be studied, as for example metal atoms, and thus very important in aeronomy. Beam experiments of course provide ion kinetic energy dependences of the cross sections from fairly high ion kinetic energies to energies substantially in excess of thermal.

ICR Ion Cyclotron Resonance

The ICR technique has now been utilized for quantitative reaction rate constant measurements for several years and is proving to be a very valuable addition to the ion chemists armory. Since the ICR technique involves low pressure experiments the possibility of excited state reactant ions exists. Rate constants can in principle be measured as a function of ion kinetic energy in ICR but most reported values are essentially at thermal energy.

D Discharge

A gaseous discharge is a somewhat unwieldy and complicated device for determining individual reaction rate constants and very few such applications have been carried out.

In a few cases, binary ion-neutral reactions give more than one set of products, usually two. In such cases two reaction channels may be given and denoted by a and b for purposes of differentiating the separate rate constants k_a and k_b or to define a branching ratio, k_a/k_b . It is often the case that the overall ion loss rate, $k_a + k_b$, is much more precisely measured than is the branching ratio. There are cases where the reaction products are undetermined and simply listed as "Products". There are also cases where no reaction was detected to give any products and this is also indicated by "products" in order to exclude all possibilities.

References: Given at the end of each Table

The references are given by the first author of the paper and the year. All the papers of a given first author and year are further sequenced by a small letter a, b, c,... etc. following the year.

Remarks: Given at the end of each Table

The data refer largely to thermal energy (thermalized room temperature measurements) but in some cases energy or temperature dependencies are available and this is so indicated in the column headed "Remarks".

In many cases reactions have been measured by more than one method and/or in more than one laboratory. Measurements which have been improved or which are otherwise considered to be obsolete or in error have not been tabulated.

TABLE I. Binary Positive-Ion Reactions

Reaction	$k(\text{cm}^3\text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{H}^+ + \text{O} \rightarrow \text{O}^+ + \text{H}$	3.8(-10)	$\pm 50\%$	FA	Fehsenfeld 1972a	a
$\text{H}^+ + \text{Fe} \rightarrow \text{Fe}^+ + \text{H}$	7.4(-9)		B	Rutherford 1972c	g
$\text{H}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{H}$	1.9(-9)	$\pm 30\%$	FA	Fehsenfeld 1972a	
$\text{H}^+ + \text{CO}_2 \rightarrow \text{COH}^+ + \text{O}$	3.0(-9)	$\pm 30\%$	FA	Fehsenfeld 1971a	
$\text{He}^+ + \text{H}_2 \rightarrow \text{products}$	< 1 (-13)		FA	Fehsenfeld 1966a	
$\left. \begin{array}{l} \text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{He} \\ \quad \quad \quad \rightarrow \text{N}_2^+ + \text{He} \end{array} \right\}$	1.2(-9)	$\pm 30\%$	FA	Farragher 1970	$k_a/k_b = 1.5$, b
	1.0(-9)	+ 0.3, -0.2	DT	Heimerl 1969	$k_a/k_b = 1.2$; c
	1.85(-9)	$\pm 15\%$	ICR	Laudenslager 1973	
	1.2(-9)	$\pm 20\%$	FA	Dunkin 1968a	d
	1.5(-9)	$\pm 30\%$	MS	Warneck 1967a	$k_a/k_b = 1.1$
$\left. \begin{array}{l} \text{He}^+ + \text{O}_2 \rightarrow \text{O}^+ + \text{O} + \text{He} \\ \quad \quad \quad \rightarrow \text{O}_2^+ + \text{He} \end{array} \right\}$			FA	Schmeltekopf 1968	$k_a/k_b = 2.2$, e
	1.45(-9)	$\pm 15\%$	SA	Sayers 1964	
	1.0(-9)	$\pm 30\%$	FA	Farragher 1970	$k_a/k_b = 1.6$
	8.5(-10)	+ 2.5, -2.0	DT	Heimerl 1969	$k_a/k_b = 4$, c
	1.5(-9)	$\pm 25\%$	ICR	Laudenslager 1973	
$\left. \begin{array}{l} \text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He} \\ \quad \quad \quad \rightarrow \text{CO}^+ + \text{O} + \text{He} \end{array} \right\}$	1.2(-9)	$\pm 30\%$	MS	Warneck 1967	
	1.10(-9)	$\pm 15\%$	SA	Sayers 1964	
	1.7(-9)	$\pm 30\%$	FA	Fehsenfeld 1966a	
	2.0(-9)	$\pm 15\%$	ICR	Laudenslager 1973	
	1.6(-9)	$\pm 30\%$	MS	Moran 1966	
$\left. \begin{array}{l} \text{He}^+ + \text{NO} \rightarrow \text{N}^+ + \text{O} + \text{He} \\ \quad \quad \quad \rightarrow \text{NO}^+ + \text{He} \end{array} \right\}$	1.7(-9)	$\pm 30\%$	FA	Fehsenfeld 1966a	
	2.1(-9)	$\pm 30\%$	MS	Moran 1966	
	2.0(-9)	$\pm 15\%$	ICR	Laudenslager 1973	
	5.6(-10)	± 0.5	FA	Howard 1970	
	4.5(-10)	$\pm 30\%$	FA	Bolden 1972	
$\left. \begin{array}{l} \text{He}^+ + \text{CO}_2 \rightarrow \text{O}^+ + \text{CO} + \text{He} \\ \quad \quad \quad \rightarrow \text{CO}^+ + \text{O} + \text{He} \end{array} \right\}$	1.2(-9)	$\pm 30\%$	FA	Fehsenfeld 1966a	
	1.6(-9)	$\pm 15\%$	ICR	Laudenslager 1973	
	1.5(-9)	$\pm 15\%$	ICR	Bowers 1972	
	2.3(-9)	$\pm 15\%$	ICR	Bowers 1972	
	1.1(-9)	$\pm 30\%$	FA	Fehsenfeld 1966b	
$\left. \begin{array}{l} \text{C}^+ + \text{O}_2 \rightarrow \text{CO}^+ + \text{O} \\ \quad \quad \quad \rightarrow \text{CO}_2^+ + \text{O} \end{array} \right\}$	9.0(-10)	$\pm 30\%$	MS	Franklin 1965	
	1.9(-9)	$\pm 30\%$	FA	Fehsenfeld 1966b	
	1.6(-9)	$\pm 30\%$	D	Schilderout 1970	

NOTE: In expressing the value of a rate constant the notation 3.8 (-10) is used to indicate 3.8×10^{-10} .

Table I Continued

Reaction	$k(\text{cm}^3 \text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{C}^+ + \text{H}_2\text{O} \rightarrow \text{COH}^+ + \text{H}$	2.0(-9)	$\pm 30\%$	FA	Bolden 1972	
$\text{N}^+ + \text{Na} \rightarrow \text{Na}^+ + \text{N}$	very small		B	Rutherford 1972a	g
$\text{N}^+ + \text{Mg} \rightarrow \text{Mg}^+ + \text{N}$	1.2(-9)		B	Rutherford 1971	g
$\text{N}^+ + \text{Ca} \rightarrow \text{Ca}^+ + \text{N}$	1.1(-9)		B	Rutherford 1972b	g
$\text{N}^+ + \text{Fe} \rightarrow \text{Fe}^+ + \text{N}$	1.5(-9)		B	Rutherford 1972c	g
$\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$	7 (-10)	$\pm 30\%$	FA	Fehsenfeld 1967a	
$\text{N}^+ + \text{CO} \rightarrow \text{CO}^+ + \text{N}$	5 (-10)	$\pm 30\%$	FA	Fehsenfeld 1967b	
$\text{N}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}$	8 (-10)	$\pm 30\%$	FA	Goldan 1966	
$\text{N}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}$ $\rightarrow \text{NO}^+ + \text{O}$	7 (-10)	$\pm 30\%$	FA	Farragher 1970	
	5 (-10)	$\pm 30\%$	DT	Johnsen 1970	h
	6 (-10)	$\pm 30\%$	FA	Dunkin 1968	d, s
	6.1(-10)	$\pm 30\%$	MS	Warneck 1967b	$k_a/k_b = 2.8$
			FA	Goldan 1966	$k_a \approx k_b$
	7 (-10)		MS	Aquilanti 1966	$k_a/k_b = 1.3$
$\text{N}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}$	2.6(-9)	± 0.4	FA	Howard 1970	
	2.6(-9)	$\pm 30\%$	FA	Bolden 1972	
$\text{N}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{N}$	1.3(-9)	$\pm 30\%$	FA	Fehsenfeld 1967b	
$\text{O}^+ + \text{H} \rightarrow \text{H}^+ + \text{O}$	6.8(-10)	$\pm 50\%$	1 and Keq	Fehsenfeld 1972a	a
$\text{O}^+ + \text{Na} \rightarrow \text{Na}^+ + \text{O}$	small		B	Rutherford 1972b	g
$\text{O}^+ + \text{Mg} \rightarrow \text{Mg}^+ + \text{O}$	small		B	Rutherford 1971	g
$\text{O}^+ + \text{Ca} \rightarrow \text{Ca}^+ + \text{O}$	7.6(-10)		B	Rutherford 1972b	g
$\text{O}^+ + \text{Fe} \rightarrow \text{Fe}^+ + \text{O}$	2.9(-9)		B	Rutherford 1972c	g
$\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$	2.0(-9)	$\pm 30\%$	FA	Fehsenfeld 1967a	
$\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$	1.3(-12)	$\pm 15\%$	FA	Schmeltekopf 1968	i
	1.2(-12)	$\pm 10\%$	FA	Dunkin 1968	
			FA	Ferguson 1969	j, s
$\text{O}^+(^2\text{D}) + \text{N}_2 \rightarrow \text{N}_2^+ + \text{O}$	~ 1 (-9)		B	Rutherford 1971	g
$\text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}$	< 1 (-12)		FA	Dunkin 1971a	
$\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$	2.0(-11)	$\pm 15\%$	FA	Dunkin 1968	
	2.0(-11)	+0.4, -0.3	SA	Copsey 1966	
			SA	Smith 1968	k
			FA	Ferguson 1969	j, k, s
	2.0(-11)	± 0.5	MS	Warneck 1967b	
$\text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO}$	1.2(-9)	$\pm 30\%$	FA	Fehsenfeld 1966c	
	1.0(-9)	$\pm 30\%$	MS	Paulson 1966	

Table I Continued

Reaction	$k(\text{cm}^3\text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{O}$	2.3(-9)	± 0.25	FA	Howard 1970	
	2.4(-9)	$\pm 30\%$	FA	Bolden 1972	
$\text{O}^+ + \text{N}_2\text{O} \rightarrow \text{N}_2\text{O}^+ + \text{O}$	2.2(-10)	± 1.3	MS	Ryan 1972	1
$\quad \rightarrow \text{NO}^+ + \text{NO}$	2.3(-10)	± 1.4	MS	Ryan 1972	
$k_a + k_b = 6.3(-10)$		$\pm 30\%$	FA	Dunkin 1971a	1
$\text{O}^+ + \text{NO}_2 \rightarrow \text{NO}_2^+ + \text{O}$	1.6(-9)	$\pm 30\%$	FA	Dunkin 1971a	
$\text{Na}^+ + \text{O}_3 \rightarrow \text{NaO}^+ + \text{O}_2$	< 1 (-11)		FA	Ferguson 1968	m
$\text{Mg}^+ + \text{O}_3 \rightarrow \text{MgO}^+ + \text{O}_2$	2.3(-10)	$\pm 50\%$	FA	Ferguson 1968	
$\text{S}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{S}$	4.2(-10)	$\pm 20\%$	FA	Fehsenfeld 1973a	
$\text{S}^+ + \text{O}_2 \rightarrow \text{SO}^+ + \text{O}$	1.6(-11)	$\pm 20\%$	FA	Fehsenfeld 1973a	
$\text{S}^+ + \text{CO}_2 \rightarrow \text{products}$	< 1 (-12)		FA	Fehsenfeld 1973a	
$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}$	6.8(-10)	$\pm 20\%$	ICR	Bowers 1969a	
	7.0(-10)	$\pm 30\%$	FA	Adams 1970	
$\text{Ar}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{Ar}$	6.6(-11)	?	MS	Warneck 1967c	n
	5 (-11)	$\pm 75\%$	ICR	Laudenslager 1973	
$\text{Ar}^+ + \text{CO} \rightarrow \text{CO}^+ + \text{Ar}$	1.2(-10)	$\pm 30\%$	MS	Warneck 1967c	
	9.0(-11)	$\pm 30\%$	FA	Fehsenfeld 1966d	
	5 (-11)	$\pm 90\%$	ICR	Laudenslager 1973	
$\text{Ar}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{Ar}$	3.9(-10)	$\pm 30\%$	MS	Warneck 1967c	
	2.5(-10)	$\pm 30\%$	ICR	Laudenslager 1973	
$\text{Ar}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{Ar}$	1.1(-10)	$\pm 30\%$	MS	Warneck 1967c	
	5.0(-11)	$\pm 30\%$	FA	Adams 1970	k
	7 (-11)	$\pm 50\%$	ICR	Laudenslager 1973	
	5.0(-11)	$\pm 25\%$	SA	Smith 1970	e
$\text{Ar}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{Ar}$ $\quad \rightarrow \text{ArH}^+ + \text{OH}$	1.4(-9)	± 0.1	FA	Howard 1970	
	1.6(-9)	$\pm 30\%$	FA	Bolden 1972	
$\text{Ar}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{Ar}$	7.0(-10)	$\pm 30\%$	MS	Warneck 1967c	
	7.6(-10)	$\pm 30\%$	FA	Fehsenfeld 1966d	
	4.6(-10)	$\pm 15\%$	ICR	Laudenslager 1973	
$\text{Ar}^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H} + \text{Ar}$	6.5(-10)	$\pm 30\%$	MS	Jones 1971	
$\quad \rightarrow \text{CH}_2^+ + \text{H}_2 + \text{Ar}$	1.4(-10)	$\pm 30\%$	MS	Jones 1971	
$k_a + k_b = 9.0(-10)$		$\pm 30\%$	FA	Bolden 1970	
$\quad \rightarrow \text{products}$	1.3(-9)	$\pm 15\%$	ICR	Bowers 1972	
$\text{Ar}^+ + \text{C}_2\text{H}_6 \rightarrow \text{products}$	1.1(-9)	$\pm 15\%$	ICR	Bowers 1972	
$\text{K}^+ + \text{O}_3 \rightarrow \text{KO}^+ + \text{O}_2$	< 1 (-11)		FA	Ferguson 1968	m

Table I Continued

Reaction	$k(\text{cm}^3\text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{Cu}^+ + \text{O}_3 \rightarrow \text{CuO}^+ + \text{O}_2$	1.6(-10)	$\pm 50\%$	FA	Ferguson 1968	
$\text{Fe}^+ + \text{O}_3 \rightarrow \text{FeO}^+ + \text{O}_2$	1.5(-10)	$\pm 50\%$	FA	Ferguson 1968	
$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$	2.0(-9)	$\pm 10\%$	MS	Reuben 1962	
	1.85(-9)		MS	Warneck 1967d	
	1.95(-9)	$\pm 20\%$	ICR	Bowers 1969b	
$\text{H}_2^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$	1.95(-9)	$\pm 20\%$	ICR	Bowers 1969a	
$\text{H}_2^+ + \text{Ar} \rightarrow \text{ArH}^+ + \text{H}$	1.2(-9)	$\pm 20\%$	ICR	Bowers 1969a	
$\text{N}_2^+ + \text{N} \rightarrow \text{N}^+ + \text{N}_2$	< 1 (-11)		FA	Ferguson 1965	
$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$	1.4(-10)	X2	FA	Fehsenfeld 1970	
$\rightarrow \text{O}^+ + \text{N}_2$	< 1 (-11)		FA	Ferguson 1965	t
$\text{N}_2^+ + \text{H}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$	1.7(-9)	$\pm 30\%$	FA	Fehsenfeld 1967a	
	1.4(-9)	$\pm 20\%$	ICR	Bowers 1969	
$\text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2$	6.6(-11)	$\pm 30\%$	FA	Farragher 1970	
	6 (-11)		DT	Johnsen 1970	b
	5 (-11)	$\pm 30\%$	FA	Ferguson 1969	j, s
	6.5(-11)	± 1	MS	Aquilanti 1966	
$\rightarrow \text{NO}^+ + \text{NO}$	< 3 (-14)		MS	Warneck 1967b	
$\text{N}_2^+ + \text{CO} \rightarrow \text{CO}^+ + \text{N}_2$	7 (-11)	$\pm 30\%$	FA	Fehsenfeld 1967b	
$\text{N}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2$	3.3(-10)	$\pm 30\%$	FA	Fehsenfeld 1970	
	4.8(-10)	$\pm 30\%$	MS	Warneck 1967b	
$\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}_2$	2.2(-9)	± 0.3	FA	Howard 1970	
$\rightarrow \text{N}_2\text{H}^+ + \text{OH}$	2.0(-9)	$\pm 30\%$	FA	Bolden 1972	
$\text{N}_2^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{N}_2$	9 (-10)	$\pm 30\%$	FA	Fehsenfeld 1967b	
$\text{N}_2^+ + \text{Na} \rightarrow \text{Na}^+ + \text{N}_2$	5.8(-10)	$\pm 50\%$	FA	Farragher 1969	
	1.9(-9)		B	Rutherford 1972a	g
$\text{N}_2^+ + \text{Mg} \rightarrow \text{Mg}^+ + \text{N}_2$	7.2(-10)		B	Rutherford 1971a	g
$\text{N}_2^+ + \text{Ca} \rightarrow \text{Ca}^+ + \text{N}_2$	1.8(-9)		B	Rutherford 1972b	g
$\text{N}_2^+ + \text{Fe} \rightarrow \text{Fe}^+ + \text{N}_2$	4.3(-10)		B	Rutherford 1972c	g
$\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$	1.8(-10)	X2	FA	Goldan 1966	
$\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$	< 1 (-15)		FA	Ferguson 1965	o
$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	6.3(-10)	$\pm 30\%$	FA	Fehsenfeld 1970	
	7.7(-10)	$\pm 30\%$	MS	Warneck 1967e	
	7.2(-10)	± 1.5	DT	Johnsen 1970	
$\text{O}_2^+ + \text{NO}_2 \rightarrow \text{NO}_2^+ + \text{O}_2$	6.6(-10)	$\pm 30\%$	FA	Fehsenfeld 1973b	
$\text{O}_2^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{O}_2$	2.4(-9)	$\pm 30\%$	FA	Fehsenfeld 1973c	
$\text{O}_2^+ + \text{Na} \rightarrow \text{Na}^+ + \text{O}_2$	6.7(-10)	$\pm 50\%$	FA	Farragher 1969	
	1.4(-9)		B	Rutherford 1972a	g

Table I Continued

Reaction	$k(\text{cm}^3 \text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{O}_2^+(\text{a}^1\Pi_u) + \text{Na} \rightarrow \text{Na}^+ + \text{O}_2$	2.0(-9)		B	Rutherford 1972a	g
$\text{O}_2^+ + \text{Na} \rightarrow \text{NaO}^+ + \text{O}$	1.2(-10)		B	Rol 1968	p
	< 7 (-11)		FA	Farragher 1969	
$\text{O}_2^+ + \text{Mg} \rightarrow \text{Mg}^+ + \text{O}_2$	1.2(-9)		B	Rutherford 1971a	g
$\text{O}_2^+(\text{a}^1\Pi_u) + \text{Mg} \rightarrow \text{Mg}^+ + \text{O}_2$	> 3 (-9)		B	Rutherford 1971a	q, g
$\text{O}_2^+ + \text{Ca} \rightarrow \text{Ca}^+ + \text{O}_2$	1.8(-9)		B	Rutherford 1972b	g
$\text{O}_2^+(\text{a}^1\Pi_u) + \text{Ca} \rightarrow \text{Ca}^+ + \text{O}_2$	3.5(-9)		B	Rutherford 1972b	g
$\text{O}_2^+ + \text{Fe} \rightarrow \text{Fe}^+ + \text{O}_2$	1.1(-9)		B	Rutherford 1972c	g
$\text{NO}^+ + \text{Na} \rightarrow \text{Na}^+ + \text{NO}$	7.7(-11)	$\pm 50\%$	FA	Farragher 1969	
$\text{NO}^+ + \text{Mg} \rightarrow \text{Mg}^+ + \text{NO}$	8.1(-10)		B	Rutherford 1971a	g
$\text{NO}^+ + \text{Ca} \rightarrow \text{Ca}^+ + \text{NO}$	4.0(-9)		B	Rutherford 1972b	g
$\text{NO}^+ + \text{Fe} \rightarrow \text{Fe}^+ + \text{NO}$	9.2(-10)		B	Rutherford 1972c	g
$\text{NO}^+ + \text{O}_3 \rightarrow \text{NO}_2^+ + \text{O}_2$	< 1 (-14)		FA	Fehsenfeld 1973b	
$\text{CO}^+ + \text{O} \rightarrow \text{O}^+ + \text{CO}$	1.4(-10)	$\pm 50\%$	FA	Fehsenfeld 1972a	
$\text{CO}^+ + \text{N} \rightarrow \text{products}$	< 2 (-11)		FA	Fehsenfeld 1972a	
$\text{CO}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{CO}$	3.3(-10)	$\pm 30\%$	FA	Fehsenfeld 1972a	
$\text{CO}^+ + \text{H}_2 \rightarrow \text{COH}^+ + \text{H}$	2.0(-9)	$\pm 30\%$	FA	Fehsenfeld 1967a	
$\text{CO}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}$	2.0(-10)	$\pm 30\%$	FA	Fehsenfeld 1966b	
$\text{CO}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{CO}$	1.1(-9)	$\pm 30\%$	FA	Fehsenfeld 1966b	
$\text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{products}$	2.2(-9)	$\pm 30\%$	FA	Bolden 1972	
$\text{SiO}^+ + \text{O} \rightarrow \text{Si}^+ + \text{O}_2$	~ 2 (-10)		FA	Fehsenfeld 1969a	
$\text{SiO}^+ + \text{N} \rightarrow \text{Si}^+ + \text{NO}$	~ 2 (-10)		FA	Fehsenfeld 1969a	
$\quad \quad \quad \rightarrow \text{NO}^+ + \text{Si}$	~ 1 (-10)		FA	Fehsenfeld 1969a	
$\text{MgO}^+ + \text{O} \rightarrow \text{Mg}^+ + \text{O}_2$	~ 1 (-10)		FA	Ferguson 1968	
$\text{SO}^+ + \text{CO} \rightarrow \text{S}^+ + \text{CO}_2$	< 1 (-12)		FA	Fehsenfeld 1973a	
$\text{H}_3^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}_2$	1.5(-9)	$\pm 30\%$	FA	Burt 1970	
	1.0(-9)	$\pm 30\%$	MS	Aquilanti 1965	
$\text{H}_3^+ + \text{CO} \rightarrow \text{COH}^+ + \text{H}_2$	1.4(-9)	$\pm 30\%$	FA	Burt 1970	
$\text{H}_3^+ + \text{NO} \rightarrow \text{NOH}^+ + \text{H}_2$	1.4(-9)	$\pm 30\%$	FA	Burt 1970	
$\text{H}_3^+ + \text{CO}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H}_2$	1.9(-9)	$\pm 30\%$	FA	Burt 1970	
$\text{H}_3^+ + \text{NO}_2 \rightarrow \text{NO}^+ + \text{OH} + \text{H}_2$	7 (-10)	$\pm 30\%$	FA	Burt 1970	
$\text{H}_3^+ + \text{N}_2\text{O} \rightarrow \text{N}_2\text{OH}^+ + \text{H}_2$	1.8(-9)	$\pm 30\%$	FA	Burt 1970	
$\text{H}_3^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{H}_2$	1.6(-9)	$\pm 30\%$	FA	Burt 1970	
	7.5(-10)	$\pm 30\%$	MS	Aquilanti 1966a	
$\text{H}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$	1.9(-9)	$\pm 30\%$	FA	Burt 1970	
$\quad \quad \quad \rightarrow \text{C}_2\text{H}_3^+ + 2\text{H}_2$	1.2(-10)	$\pm 30\%$	FA	Burt 1970	

Table 1 Continued

Reaction	k(cm ³ sec ⁻¹)	Uncertainty	Method	Reference	Remarks
$H_3^+ + C_2H_2 \rightarrow C_2H_3^+ + H_2$	1.9(-10)	± 30%	FA	Burt 1970	
$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	~ 3.0(-9)		FA	Burt 1970	
$H_3^+ + NH_3 \rightarrow NH_4^+ + H_2$	~ 3.6(-9)		FA	Burt 1970	
$N_2H^+ + CO_2 \rightarrow CO_2H^+ + N_2$	9.2(-10)	± 30%	FA	Burt 1970	
$N_2H^+ + N_2O \rightarrow N_2OH^+ + N_2$	7.9(-10)	± 30%	FA	Burt 1970	
$N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2$	8.9(-10)	± 30%	FA	Burt 1970	
$N_2H^+ + H_2O \rightarrow H_3O^+ + N_2$	~ 5 (-10)		FA	Burt 1970	
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	1.7(-9)	± 30%	FA	Bolden 1972	
	1.8(-9)	± 30%	MS	Good 1970	
	1.6(-9)	± 20%	MS	Gupta 1967	
$H_2O^+ + Na \rightarrow Na^+ + H_2O$	1.9(-9)		B	Rutherford 1972a	g
$H_2O^+ + Ca \rightarrow Ca^+ + H_2O$	4.0(-9)		B	Rutherford 1972b	g
$H_2O^+ + Fe \rightarrow Fe^+ + H_2O$	1.5(-9)		B	Rutherford 1972c	g
$CO_2^+ + H \rightarrow HCO^+ + O$ $\rightarrow H^+ + CO_2$	6 (-10)	± 50%	FA	Fehsenfeld 1971a	$k_a/k_b \sim 5$
$CO_2^+ + O \rightarrow O_2^+ + CO$ $\rightarrow O^+ + CO_2$	2.6(-10)	x 2	FA	Fehsenfeld 1970	$k_a/k_b \sim 1.7$
$CO_2^+ + N \rightarrow \text{products}$	< 1 (-11)		FA	Fehsenfeld 1970	
$CO_2^+ + H_2 \rightarrow CO_2H^+ + H$	1.4(-9)	± 30%	FA	Fehsenfeld 1967a	
$CO_2^+ + NO \rightarrow NO^+ + CO_2$	1.2(-10)	± 30%	FA	Fehsenfeld 1970	
$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$	5.0(-11)	± 30%	FA	Fehsenfeld 1970	
$NO_2^+ + NO \rightarrow NO^+ + NO_2$	2.9(-10)	± 30%	FA	Fehsenfeld 1969b	
$SO_2^+ + CO \rightarrow SO^+ + CO_2$	3.0(-10)	± 20%	FA	Fehsenfeld 1973a	
$SO_2^+ + O_2 \rightarrow O_2^+ + SO_2$	2.8(-10)	± 20%	FA	Fehsenfeld 1973a	
$H_3O^+ + Ca \rightarrow Ca^+ + H_2O + H$	4.4(-9)		B	Rutherford 1972b	g
$N_4^+ + O_2 \rightarrow O_2^+ + 2N_2$	4 (-10)	± 30%	FA	Dunkin 1971b	
$O_4^+ + O \rightarrow O_2^+ + O_3$	3 (-10)	± 2	FA	Fehsenfeld 1972b	
$O_4^+ + H_2O \rightarrow O_2^+ \cdot H_2O + O_2$	1.5(-9)	± 0.5	FA	Howard 1972	
	1.3(-9)	± 50%	MS	Good 1970	
	2.2(-9)	± 50%	FA	Fehsenfeld 1971b	
$O_2^+ \cdot N_2 + H_2O \rightarrow O_2^+ \cdot H_2O + N_2$	4 (-9)	± 2	FA	Howard 1972	
$O_2^+ \cdot N_2 + O_2 \rightarrow O_4^+ + N_2$	> 5 (-11)		FA	Adams 197b	80°K
$H_3O^+ \cdot OH + H_2O \rightarrow H_3O^+ \cdot H_2O + OH$	1.4(-9)	± 0.5	FA	Howard 1972	
	> 1 (-9)		MS	Good 1970	
	~ 3.2(-9)		FA	Fehsenfeld 1971b	

Table I Continued

Reaction	k(cm ³ sec ⁻¹)	Uncertainty	Method	Reference	Remarks
$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$	1.0(-9)	± 0.4	FA	Howard 1972	
	9 (-10)	± 50%	MS	Good 1970	
	1.9(-9)	± 50%	FA	Fehsenfeld 1971b	
$- H_3O^+ + OH + O_2$	2 (-10)	± 1	FA	Howard 1972	
	3 (-10)	± 1	MS	Good 1970	
	≤ 3 (-10)		FA	Fehsenfeld 1971b	
$NO^+ \cdot CO_2 + H_2O \rightarrow NO^+ \cdot H_2O + CO_2$	~ 1 (-9)		FA	Dunkin 1971b	
$NO^+(H_2O)_3 + H_2O \rightarrow H_3O^+(H_2O)_2 + HNO_2$	7 (-11)	± 2	FA	Howard 1972	
	8 (-11)	± 50%	FA	Fehsenfeld 1971c	
	7 (-11)	± 30%	SA	Puckett 1971a	r
$NO^+ \cdot NO + H_2O \rightarrow NO^+ \cdot H_2O + NO$	1.4(-9)	± 0.3	SA	Puckett 1971a	
$NO^+ \cdot NO + NH_3 \rightarrow NO^+ \cdot NH_3 + NO$	1.3(-9)	± 0.2	SA	Puckett 1971a	
$NO^+ \cdot H_2O + NO \rightarrow NO^+ \cdot NO + H_2O$	9 (-14)	± 2	SA	Puckett 1971a	
$NO^+ \cdot H_2O + NH_3 \rightarrow NH_4^+ + HNO_2$	1.0(-9)	± 30%	FA	Fehsenfeld 1971d	
$NO_2^+ \cdot H_2O + NH_3 \rightarrow NH_4^+ + HNO_3$	1.1(-9)	± 30%	FA	Fehsenfeld 1973c	
$NO^+ \cdot NH_3 + NH_3 \rightarrow NH_4^+ + ONNH_2$	9.1(-10)	± 30%	SA	Puckett 1971b	
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	1.9(-9)	± 0.2	ICR	Huntress 1971a	
	1.5(-9)	± 30%	MS	Melton 1966	
	1.7(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	2.1(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+(H_2O) + NH_3 \rightarrow \text{products}$	2.6(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+(H_2O)_2 + NH_3 \rightarrow \text{products}$	1.6(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+(H_2O)_3 + NH_3 \rightarrow \text{products}$	2.1(-9)	± 30%	FA	Fehsenfeld 1973c	
$NH_4^+(H_2O) + NH_3 \rightarrow NH_4^+(NH_3) + H_2O$	1.2(-9)	± 30%	FA	Fehsenfeld 1973c	
$NH_4^+(H_2O)_2 + NH_3 \rightarrow NH_4^+(NH_3)(H_2O) + H_2O$	≥ 9 (-10)	± 30%	FA	Fehsenfeld 1973c	

FOOTNOTES

- a) Agrees well with extrapolated beam measurements
- b) Farragher gives $k_a = 6.5(-10) \pm 1.3$, $k_b = 4.2(-10) \pm 0.9$
- c) Heimerl gives k as a function of ion kinetic energy to ~ 0.1 eV
- d) Rate constant found to be independent of temperature, 300-600 K
- e) Rate constant proportional to T^{-1} in thermal range
- f) Rate constant independent of N_2 vibrational temperature from 300-600^oK but ratio k_a/k_b increases with T_v
- g) Extrapolated from beam energies. This leads to additional uncertainty in k , probably reliable to within factor of 2.
- h) Johnsen gives k as function of ion kinetic energy to ~ 1 eV
- i) Schmeltekopf gives k as function of N_2 vibrational temperature from 300-6000 K
- j) Rate constant given for temperature range 80-600 K
- k) Gives rate constant proportional to $T^{-\frac{1}{2}}$ in thermal range.
- l) Ryan gives $k_a + k_b = 4.3(-10) \pm 0.6$. Dunkin 1971 erroneously neglects channel b
- m) Probably endothermic
- n) Measurements on this reaction have given rate constants ranging from $4(-12)$ to $6.6(-11)$, depending on experimental conditions. This is almost surely due to the near resonance involved and the difficulties are elaborated in Adams 1970b where a pressure dependent k is observed. This is also discussed by Adams, Dean, and Smith, Int. J. Mass Spectrometry and Ion Phys. 10, 63, 1972.
- o) It has also been shown (FA) that $k < 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$ at 600 K
- p) More details of this experiment, including the rate constant cited are given by Rol and Entemann in a General Dynamics/Convair Report GDC-DBE69-002 of January 1969
- q) Rate constant is not given but cross section data down to 10 eV shows clearly that rate constant is quite large
- r) Reaction is endothermic
- s) The energy dependence of this reaction is given in McFarland, et al, J. Chem. Phys. 60, Jan. 1, 1974. (The full reference is M. McFarland, D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson and A. L. Schmeltekopf, and all known data is summarized in figures in this paper).
- t) Current measurements in progress suggest that this rate constant may be slightly larger than 10^{-11}

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4.4.3 TABLE II. Binary Negative-Ion Reactions

Reaction	k(cm ³ sec ⁻¹)	Uncertainty	Method	Reference	Remarks
H ⁻ + H → H ₂ + e	1.3(-9)	± 50%	FA	Schmeltekopf 1967	a
	1.8(-9)	X2	FA	Fehsenfeld 1973a	
H ⁻ + CO → HCO + e	~ 5 (-11)		FA	Dunkin, 1970	
H ⁻ + NO → HNO + e	4.6(-10)	± 30%	FA	Dunkin, 1970	
H ⁻ + O ₂ → HO ₂ + e	1.2(-9)	± 0.2	FA	Dunkin, 1970	
→ O ⁻ + OH	< 1 (-11)		FA	Dunkin, 1970	
→ O ₂ ⁻ + H	< 1 (-11)		FA	Dunkin, 1970	
→ OH ⁻ + O	< 1 (-11)		FA	Dunkin, 1970	
H ⁻ + N ₂ O → OH ⁻ + N ₂	1.1(-9)	± 0.3	FA	Dunkin, 1970	
H ⁻ + NO ₂ → NO ₂ ⁻ + H	2.9(-9)	± 30%	FA	Ferguson, 1969	
H ⁻ + H ₂ O → OH ⁻ + H ₂	3.8(-9)	± 30%	MS	Melton, 1971	
C ⁻ + H ₂ → products	< 1 (-13)		FA	Fehsenfeld 1970	
C ⁻ + CO → C ₂ O + e	4.1(-10)	± 30%	FA	Fehsenfeld, 1970	
C ⁻ + O ₂ → O ⁻ + CO	4.0(-10)	± 30%	FA	Fehsenfeld, 1970	
C ⁻ + N ₂ O → CO + N ₂ + e	9.0(-10)	± 30%	FA	Fehsenfeld, 1970	
C ⁻ + CO ₂ → 2CO + e	4.7(-11)	± 30%	FA	Fehsenfeld, 1970	
O ⁻ + O → O ₂ + e	1.9(-10)	X2	FA	Fehsenfeld, 1967	
O ⁻ + N → NO + e	2.2(-10)	X2	FA	Fehsenfeld, 1967	
O ⁻ + H ₂ → H ₂ O + e	7.0(-10)	± 0.5	DT	Parkes, 1972a	
	6.0(-10)	± 30%	FA	Ferguson, 1969	
	7.2(-10)	± 1	DT	Moruzzi, 1968	
→ OH ⁻ + H	3.3(-11)	± 0.5	DT	Parkes, 1972a	
O ⁻ + CO → CO ₂ + e	6.5(-10)	± 1	DT	Moruzzi, 1968	
	4.4(-10)	± 30%	FA	Ferguson, 1969	
	7.3(-10)	± 0.7	DT	Parkes, 1972a	
O ⁻ + NO → NO ₂ + e	2.2(-10)	± 0.5	DT	Moruzzi, 1968	
	1.6(-10)	± 30%	FA	Ferguson, 1969	
O ⁻ + N ₂ → N ₂ O + e	< 5 (-13)		DT	Moruzzi, 1968	c
	< 1 (-12)		FA	Fehsenfeld, 1966	
O ⁻ + O ₂ (¹ Δ _g) → O ₃ + e	~ 3 (-10)		FA	Fehsenfeld, 1969a	
O ⁻ + H ₂ O → OH ⁻ + OH	1.4(-9)	± 30%	MS	Melton, 1971	b
O ⁻ + N ₂ O → NO ⁻ + NO	2.2(-10)	± 0.4	FA	Marx, 1973	d
	2.5(-10)	± 0.5	ICR	Marx, 1973	
	1.95(-10)	± 0.06	DT	Parkes 1973	
O ⁻ + NO ₂ → NO ₂ ⁻ + O	1.2(-9)	± 30%	FA	Ferguson, 1969	
O ⁻ + O ₃ → O ₃ ⁻ + O	5.3(-10)	X2	FA	Ferguson, 1969	
O ⁻ + CH ₄ → OH ⁻ + CH ₃	1.1(-10)	± 0.1	DT	Parkes, 1972a	
	1.0(-10)	± 20%	FA	Bohme, 1969	

Table II continued

Reaction	k (cm ³ sec ⁻¹)	Uncertainty	Method	Reference	Remarks
$O^- + C_2H_4 \rightarrow C_2H_4O + e$	4.05(-10)	± 0.5	DT	Parkes, 1972a	
$\rightarrow C_2H_2^- + H_2O$	1.9(-10)	± 0.3	DT	Parkes, 1972a	
$O^- + C_2H_2 \rightarrow C_2H_2O + e$	1.3(-9)	± 0.09	DT	Parkes, 1972a	
$\rightarrow C_2H^- + OH$	8.0(-10)	± 0.5	DT	Parkes, 1972a	
$\rightarrow C_2OH + H$	8 (-11)	± 1	DT	Parkes, 1972a	
$O^- + C_2H_6 \rightarrow OH^- + C_2H_5$	7.0(-10)	± 20%	FA	Bohme, 1969	
$O^- + C_3H_8 \rightarrow OH^- + C_3H_7$	9.3(-10)	± 20%	FA	Bohme, 1969	
$O^- + n - C_4H_{10} \rightarrow OH^- + C_4H_9$	1.2(-9)	± 20%	FA	Bohme, 1969	
$F^- + H \rightarrow HF + e$	1.6(-9)	X2	FA	Fehsenfeld, 1973a	
$S^- + H_2 \rightarrow H_2S + e$	< 1 (-15)		FA	Fehsenfeld, 1969b	
$S^- + O_2 \rightarrow SO_2 + e$	3.0(-11)	± 30%	FA	Fehsenfeld, 1969b	
$Cl^- + H \rightarrow HCl + e$	9.0(-10)	X2	FA	Ferguson, 1969	
	1.0(-9)	X2	FA	Fehsenfeld, 1973a	
$OH^- + H \rightarrow H_2O + e$	1.0(-9)	X2	FA	Ferguson, 1969	
	1.8(-9)	X2	FA	Fehsenfeld, 1973a	
$OH^- + O \rightarrow HO_2 + e$	2.0(-10)	± 50%	FA	Fehsenfeld, 1966	
$OH^- + N \rightarrow HNO + e$	< 1 (-11)		FA	Fehsenfeld, 1966	
$OH^- + NO_2 \rightarrow NO_2^- + OH$	1.9(-9)	± 30%	FA	Ferguson, 1969	
$HS^- + H \rightarrow H_2S + e$	1.3(-9)	X2	FA	Fehsenfeld, 1973a	
$CN^- + H \rightarrow HCN + e$	8.0(-10)	X2	FA	Fehsenfeld, 1973a	
$NO^- + O_2 \rightarrow O_2^- + NO$	5.0(-10)	± 30%	FA	McFarland, 1972	e
$NO^- + H_2O \rightarrow NO_2^- + N_2$	2.8(-14)	± 0.2	DT	Parkes, 1973	
$NO^- + NO_2 \rightarrow NO_2^- + NO$	7.4(-10)	± 30%	DT	McFarland, 1972	
$\dot{O}_2^- + H \rightarrow \text{products}$	1.5(-9)	X2	FA	Fehsenfeld, 1973a	
$O_2^- + N \rightarrow NO_2 + e$	4.0(-10)	± 50%	FA	Fehsenfeld, 1967	
$O_2^- + O \rightarrow O_3 + e$	3.3(-10)	± 50%	FA	Fehsenfeld, 1967	
$O_2^- + H_2 \rightarrow \text{products}$	< 1 (-12)		FA	Fehsenfeld, unpublished	
$O_2^- + O_2(^1\Delta_g) \rightarrow 2O_2 + e$	~ 2 (-10)		FA	Fehsenfeld, 1969a	
$O_2^- + N_2O \rightarrow O_3^- + N_2$	< 1 (-12)		DT	Parkes, 1973	
$O_2^- + NO_2 \rightarrow NO_2^- + O_2$	8.0(-10)	± 30%	FA	Ferguson, 1969	
$O_2^- + O_3 \rightarrow O_3^- + O_2$	3.0(-10)	± 30%	FA	Fehsenfeld, 1967	
$O_2^- + SO_2 \rightarrow SO_2^- + O_2$	4.8(-10)	± 30%	FA	Fehsenfeld, 1973b	
$NO_2^- + H \rightarrow OH^- + NO$	3.0(-10)	X2	FA	Fehsenfeld, 1972	
	4.0(-10)	X2	FA	Fehsenfeld, 1973a	
$NO_2^- + O \rightarrow \text{products}$	< 1 (-11)		FA	Fehsenfeld, unpublished	
$NO_2^- + N \rightarrow \text{products}$	< 1 (-11)		FA	Fehsenfeld, unpublished	

Table II continued

Reaction	$k(\text{cm}^3 \text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{NO}_2^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}$	~ 4 (-12)		FA	Fehsenfeld, 1969c	
$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$	1.8(-11)	$\pm 50\%$	FA	Fehsenfeld, 1968	
$\text{O}_3^- + \text{H} \rightarrow \text{OH}^- + \text{O}_2$	8.4(-10)	X2	FA	Fehsenfeld, 1973a	
$\text{O}_3^- + \text{N}_2 \rightarrow \text{products}$	< 1 (-15)		FA	Fehsenfeld, unpublished	
$\text{O}_3^- + \text{NO} \rightarrow \text{products}$	1.0(-11)	$\pm 50\%$	FA	Fehsenfeld, 1967	f
$\text{O}_3^- + \text{CO}_2 \rightarrow \text{CO}_3^- + \text{O}_2$	4.0(-10)	$\pm 30\%$	FA	Fehsenfeld, 1967	
	5.5(-10)	± 0.5	DT	Parkes, 1972b	
$\text{O}_3^- + \text{NO}_2 \rightarrow \text{products}$	2.8(-10)	$\pm 30\%$	FA	Dunkin, 1972	
$\text{O}_3^- + \text{SO}_2 \rightarrow \text{SO}_3^- + \text{O}_2$	1.7(-9)	$\pm 30\%$	FA	Fehsenfeld, 1973b	
$\text{CO}_3^- + \text{O} \rightarrow \text{O}_2^- + \text{CO}_2$	8.0(-11)	$\pm 50\%$	FA	Fehsenfeld, 1967	
$\text{CO}_3^- + \text{NO} \rightarrow \text{NO}_2^- + \text{CO}_2$	9.0(-12)	X2	FA	Fehsenfeld, 1967	
	1.8(-11)	$\pm 30\%$	FA	Fehsenfeld, 1973b	
$\text{CO}_3^- + \text{NO}_2 \rightarrow \text{products}$	2 (-10)	X2	FA	Fehsenfeld, 1973b	
$\text{CO}_3^- + \text{SO}_2 \rightarrow \text{SO}_3^- + \text{CO}_2$	2.3(-10)	$\pm 30\%$	FA	Fehsenfeld, 1973b	
$\text{NO}_3^- + \text{N} \rightarrow \text{products}$	< 1 (-11)		FA	Fehsenfeld, 1969c	
$\text{NO}_3^- + \text{O} \rightarrow \text{products}$	< 1 (-11)		FA	Fehsenfeld, 1969c	
$\text{O}_4^- + \text{O} \rightarrow \text{O}_3^- + \text{O}_2$ $\rightarrow \text{O}^- + 2\text{O}_2$	} 4.0(-10)	$\pm 50\%$	FA	Fehsenfeld, 1969c	$k_a > k_b$
$\text{O}_4^- + \text{CO} \rightarrow \text{CO}_3^- + \text{O}_2$	< 2 (-11)		FA	Adams, 1970	
$\text{O}_4^- + \text{NO} \rightarrow \text{NO}_3^{*-} + \text{O}_2$	2.5(-10)	$\pm 30\%$	FA	Adams, 1970	h
$\text{O}_4^- + \text{CO}_2 \rightarrow \text{CO}_4^- + \text{O}_2$	4.3(-10)	$\pm 30\%$	FA	Adams, 1970	
$\text{O}_4^- + \text{H}_2\text{O} \rightarrow \text{O}_2^- \cdot \text{H}_2\text{O} + \text{O}_2$	1.5(-9)		MS	Payzant, 1972	
	1.4(-9)		DT	Pack, 1971	
$\text{CO}_4^- + \text{O} \rightarrow \text{CO}_3^- + \text{O}_2$ $\rightarrow \text{O}_3^- + \text{CO}_2$	} 1.5(-10)	$\pm 50\%$	FA	Fehsenfeld, 1969c	$k_a > k_b$
$\text{CO}_4^- + \text{NO} \rightarrow \text{NO}_3^{*-} + \text{CO}_2$	4.8(-11)	$\pm 30\%$	FA	Fehsenfeld, 1969c	h
$\text{O}_2^- \cdot \text{H}_2\text{O} + \text{NO} \rightarrow \text{NO}_3^- + \text{H}_2\text{O}$	3.1(-10)	$\pm 30\%$	FA	Adams, 1970	
$\text{O}_2^- \cdot \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CO}_4^- + \text{H}_2\text{O}$	5.8(-10)	$\pm 30\%$	FA	Adams, 1970	
$\text{O}_2^- \cdot \text{H}_2\text{O} + \text{O}_3 \rightarrow \text{products}$	3 (-10)	$\pm 30\%$	FA	Fehsenfeld, 1973b	
$\text{O}_2^-(\text{H}_2\text{O})_2 + \text{O}_3 \rightarrow \text{products}$	3.4(-10)	$\pm 30\%$	FA	Fehsenfeld, 1973b	
$\text{NO}_3^{*-} + \text{NO} \rightarrow \text{NO}_2^- + \text{NO}_2$	1.5(-11)	X2	FA	Adams, 1970	h
$\text{NO}_3^- + \text{NO} \rightarrow \text{NO}_2^- + \text{NO}_2$	~ 3 (-15)		DT	Parkes, 1972c	1
$\text{O}_2^- \cdot \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{O}_4^- + \text{H}_2\text{O}$	2.5(-15)	± 1	DT	Parkes, 1971	1
$\text{O}_3^-(\text{H}_2\text{O}) + \text{CO}_2 \rightarrow \text{products}$	3 (-10)	X2	FA	Fehsenfeld, 1973b	
$\text{O}_3^-(\text{H}_2\text{O})_2 + \text{CO}_2 \rightarrow \text{products}$	2 (-10)	X2	FA	Fehsenfeld, 1973b	

Table II continued

Reactions	$k(\text{cm}^3 \text{sec}^{-1})$	Uncertainty	Method	Reference	Remarks
$\text{CO}_3^-(\text{H}_2\text{O}) + \text{HO} \rightarrow \text{products}$	1.8(-11)	X2	FA	Fehsenfeld, 1973b	
$\text{CO}_3^-(\text{H}_2\text{O}) + \text{NO}_2 \rightarrow \text{products}$	1.5(-10)	X2	FA	Fehsenfeld, 1973b	
$\text{NO}_2^-(\text{H}_2\text{O}) + \text{SO}_2 \rightarrow \text{NO}_2^-(\text{SO}_2) + \text{H}_2\text{O}$	1.5(-9)	$\pm 30\%$	FA	Fehsenfeld, 1973b	
$\text{SO}_4^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{SO}_2 + \text{O}_2$	2.5(-10)	X2	FA	Fehsenfeld, 1973b	
$\rightarrow \text{NO}_3^- + \text{SO}_3$	1 (-10)	X2	FA	Fehsenfeld, 1973b	
$\text{SO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{e}$	< 1 (-12)		FA	Fehsenfeld, 1973b	J

FOOTNOTES

- a) There is a theoretical value for k by J. C. Browne and A. Dalgarno, J. Phys. B. (Atomic and Molec. Phys. 2, 885, 1969). The value at thermal energy is $2.0(-9)$ and the energy dependence is also given.
- b) k independent of ion energy, 0-5 eV.
- c) F. Kaufman, J. Chem. Phys. 46, 2449, 1967 points out that a detailed balancing argument can be used to calculate $k < 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ from dissociative electron attachment data for N_2O .
- d) Because this reaction has often been measured with energetic O^- ions for which the rate constant is lower than for thermal ions, there has been a spread in published rate constants. This effect leads to a pressure dependence for k when the O^- is produced from N_2O as has usually been the case. This problem is resolved in Marx 1973 and all earlier measurements are rationalized.
- e) The electron affinity of NO is so low ($\sim 0.024 \text{ eV} \approx kT$) that collisional detachment is rapid in almost all gases. Such data for a number of gases are given in McFarland 1972.
- f) Products reported to be $\text{NO}_3^- + \text{O}$ in reference. This is uncertain, it is more likely that products are $\text{NO}_2^- + \text{O}_2$.
- g) Products uncertain, either NO_2^- or NO_3^- or both.
- h) There are two forms of NO_3^- , suggested as being the stable nitrate ion $\text{O}-\text{N}-\text{O}^-$ and the higher energy peroxide ion $\text{O}-\text{N}-\text{O}-\text{O}^-$ (which is denoted NO_3^{-*}).

$\begin{array}{c} | \\ \text{O} \end{array}$
- i) Reaction is endothermic
- j) Probably endothermic.

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